BULLETIN OF THE ACADEMY OF SCIENCES OF THE USSR
DIVISION OF CHEMICAL SCIENCES

1952

Index

IN ENGLISH TRANSLATION

CONSULTANTS BUREAU
152 West 42nd St., New York 18, N.Y.

—An agency for the interpretation of international knowledge

SECTIONS

Page

Table of Contents, 1952 1
Author Index, 1952 8
Subject Index, 1952 15
Index and Empirical Formulas of Organic Compounds, 1952 31

Any of the articles listed herein may be purchased separately, exactly as they appear in the published translation, for $7.50. Individual issues may be purchased for $20.00 each. The price of the translation of the entire volume is $80.00.

When ordering articles, please cite the pagination of the English translation. Direct your orders to:

CONSULTANTS BUREAU
152 West 42nd Street
New York 36, N.Y.

BULLETIN OF THE ACADEMY OF SCIENCES OF THE USSR

DIVISION OF CHEMICAL SCIENCES

1952

Index

Publication of the Academy of Sciences of the U.S.S.R.

IN ENGLISH TRANSLATION

Copyright, 1955

CONSULTANTS BUREAU

152 West 42nd Street
New York 36, N.Y.

Printed in the United States

Annual subscription $80.00
Index $ 5.00

BLANK
PAGE

TABLE OF CONTENTS

1952

January-February

	Page	Russ. page
Ninety Years of A.M.Butlerov's Theory of Chemical Structure. A.E.Arbuzov	1	3
The Development of Organic Chemistry in the Light of A.M.Butlerov's Teaching. B.A.Arbuzov	13	14
Phenol Compounds of the Inert Gases and Their Analogs. B.A.Nikitin and M.P.Kovalskaya	23	24
Experimental Study of the Electron Density in Crystals. Communication 5. Electron Density of Mg_2Si. N.V.Ageev and L.N.Guseva	31	31
Kinetics of the Polymerization of Compounds Containing a Conjugated Link. Polymerization of Methyl Acrylate. P.S.Shantarovich	41	40
Investigation of Solubility in the Reciprocal System $CaSO_4-KCl-H_2O$ at 55°. V.N.Sveshnikova	45	44
Catalytic Oxidation of Ethylene on Magnesium Chromite. L.Ya.Margolis and O.M.Todes	55	52
The Theory of Chromatography on Heterogeneous Surfaces. Communication 1. Determination from Desorption Curves of the Function Expressing the Distribution with Respect to Their Heats of Adsorption of Sites on a Solid Surface. S.Z.Roginsky and M.I.Yanovsky	63	59
The Theory of Chromatography on Heterogeneous Surfaces. Communication 3. Dynamics of the Adsorption of Mixtures on Heterogeneous Surfaces. S.Z.Roginsky and M.I.Yanovsky	69	64
New Method of Synthesizing Trialkoxytitanium Chlorides. O.V.Nogina, R.Kh. Freidlina, and A.N. Nesmeyanov	81	74
Stereoisomeric Sodium Enolates. A.N. Nesmeyanov, B.A.Sazonova, and E.I.Vasilyeva	89	78
Synthesis of Isoxazoles from β-Chlorovinyl Ketones. N.K.Kochetkov, A.N.Nesmeyanov, and N.A.Semenov	97	87
Synthesis of Aromatic Organo-Antimony Compounds by the Aid of Arylazoformates. O.A.Reutov and O.A.Ptitsyna	103	93
Investigations Relating to β-Amino Acids. Synthesis and Reactions of β-Aminobutyric Acid. V.M.Rodionov and N.G.Yartseva	113	103
Synthesis and Characterization of β-(β-Naphthyl)-β-aminopropionic Acid and of Certain of Its Derivatives. Communication 1. V.M.Rodionov and B.I.Kurtev	123	113
Synthesis of 7-Benz[a]anthracenemethanephosphonic and 12-Methyl-7-benz[a]anthracenemethanephosphonic Acids. B.A.Arbuzov and N.P.Grechkin	131	121
Investigation of Anthracene Derivatives. Communication 10. The Relative Activities of the Meso-Carbon Atoms of Anthracene and of 9,10-Dichloroanthracene in Reactions with Oxidizing Agents. B.P.Fedorov and N.V.Ptitsina	135	124
Reactions of Methylcyclohexane and Toluene in Contact with Aluminum Chloride. N.I.Shuikin and L.M.Feofanova	149	137
The Catalytic Hydrocondensation of Carbon Monoxide with Olefins. Communication 7. Effect of the Carbon Monoxide Concentration on the Hydrocondensation Reactions of Carbon Monoxide with Propene and with n-Butene. Ya.T.Eidus, N.D.Zelinsky, K.V.Puzitsky, and N.I.Ershov	157	145

Page Rus. page

The Splitting Off of the Elements of Hydrogen Halide from Monohalo Derivatives of Hydrocarbons of the Series C_nH_{2n+2}. A.P.Meshcheryakov and L.V.Petrova 165 152

Isomerization of Alkanes in Presence of $AlCl_3$ under a Pressure of Hydrogen. Communication 1. Isomerization of n-Hexane. M.G.Gonikberg, A.E.Gavrilova, and B.A.Kazansky . . . 171 157

Kinetics of the Dehydration of Alcohols in Presence of Tricalcium Phosphate. L.Kh Freidlin and A.M.Levit 177 163

The Synthesis and Reactions of Vinyl Ethers of Ethanolamines. Communication 2. The Synthesis of Aminoacetals. M.F.Shostakovsky, I.A.Chekulaeva, and N.A.Gershtein 185 172

Macromolecular Compounds. Communication 43. Significance of Acidolysis in the Polyesterification Reaction. V.V.Korshak and S.V.Vinogradova 193 180

Chemical Changes Produced in the Cellulose Macromolecule by Oxidizing Agents. Communication 6. The Presence in Oxycelluloses of Carbonic Ester Groupings and Their Effect on the Estimation of Uronic Carboxyl Groups. E.D.Kaverzneva, V.I.Ivanov, and A.S.Salova 199 185

Discussion

Answer to the Critics of the New Structural Theory. G.V.Chelintsev 205 190

"Contact Bonds" and the "New Structural Theory". A.N.Nesmeyanov. 215 196

Chronicle

Conference on the problem of the relation between chemical structure and pharmacological activity. 223 201

Conference on the basic problems of photographic science 225 202

March-April

On the 75th Birthday of Academician E.V.Britske 237 209

General and Inorganic Chemistry

The Periodic Law of D.I.Mendeleev and the Stability of Coordination Compounds. A.A. Grinberg and K.B.Yatsimirsky 239 211

Thermochemistry and Structure of Atoms. Communication 6. Thermochemistry of Boron: Application of the Rule of Thermochemical Logarithmics to Elements of the Third Group of D.I.Mendeleev's System. A.F.Kapustinsky and O.Ya.Samoilov. 245 218

Micro-Hardness Method of Studying Intracrystalline Liquation. D.A.Petrov and L.A.Raikovskaya 251 225

Thermodynamic Study of the Systems Cadmium – Zinc, Cadmium – Lead, Cadmium – Tin, Bismuth – Cadmium, Tin – Zinc, and Lead – Tin. V.S.Lyashenko 255 230

Kinetics of Polymerization of Compounds with Conjugated Double Bonds. Polymerization of Methyl Acrylate in Absence of Light. P.S.Shantarovich 265 243

A New Class of Coordination Compounds of Chromium with Amino Acids. L.M.Volshtein 269 248

Organic and Biological Chemistry

Addition Reactions of Perfluoro-Olefins. I.L.Knunyants and A.V.Fokin 279 261

β-(β'-Naphthyl)-β-aminopropionic Acid and Its Pyrimidine Derivatives. Communication 2. V.M.Rodionov and B.I.Kurtev 285 268

Synthesis of β-Amino-β-cyclohexylpropionic Acid and of Some of Its Derivatives. V.M. Rodionov and T.S.Kiseleva 293 278

Page Russ. page

Synthesis of Polycyclic Compounds Related to the Steroids. XI. Researches on the Stereochemistry of Cyclic Compounds. I. Condensation of Divinyl with Citraconic and Mesaconic Acids and Their Esters. Cis-Trans-Isomerism of 1-Methylcyclohexane-1,2-dicarboxylic Acids and Their Esters. I.N.Nazarov and V.F.Kucherov 301 289

Synthesis of Steroid Compounds and of Related Substances. XII. Condensation of Cyclic β-Diketones with Vinyl Ketones, and Transformations of the Resulting Products. I.N.Nazarov and S.I.Zavyalov 309 300

Synthesis of Hydrocarbons of the Cyclobutane Series. Communication 2. 1-Methyl-3-ethylcyclobutane and Di-(3-methylcyclobutyl)-methane. B.A.Kazansky and M.Yu. Lukina 319 314

Effect of the Dimensions of the Elementary Crystallites on the Porosity and Activity of Al_2O_3 Catalysts of Dehydration Reactions. A.M.Rubinshtein, V.E.Vasserberg, and N.A.Pribytkova 325 323

Optical Activity of Cellulose Triacetate. N.M.Bazhenov and M.V.Volkenshtein. 333 334

Reactions of Diene Hydrocarbons with Nitroso Compounds. Addition of Buta-1,3-diene to Nitrosobenzene. Communication 1. Yu. A. Arbuzov. 339 344

Studies of Quinoline Derivatives. Communication 1. N-Aryl Quaternary Salts of Quinoline Derivatives. G.T.Pilyugin 347 353

Brief Communications

Reactions of Diene Hydrocarbons with Nitroso Compounds. Reaction of Buta-1,3-diene, 2,3-Dimethylbuta-1,3-diene, and Cyclohexa-1,3-diene with 1-Chloro-1-nitrosocyclohexane. Yu.A.Arbuzov and A. Markovskaya. 355 363

Discussion

Distribution of π-Electron Density and Interatomic Distances. 2. G.V.Bykov. 359 367

Chronicle

240th Anniversary of the Birth of M.V.Lomonosov 367 375

Award of D.I.Mendeleev Prizes for 1951 . . . . 373 379

May-June

Inorganic and Physical Chemistry

Electrochemical Behavior of Iron in Oxidizing Media. Communication 3. Cathodic Polarization of Iron in Oxidizing Media. L.Ya.Gurvich and G.V.Akimov. 377 385

Mechanical Properties of Alloys of the Magnesium – Cadmium System. E.M.Savitsky and V.V.Baron 383 392

Coordination Numbers and Hydration of the Ions Li^+, Na^+, K^+, Cl^-, Br^- and I^- in Aqueous Solutions O. Ya. Samoilov 389 398

The Natural Sorbents of the Far East. Communication 1. Electron-Microscope Investigations of Natural Sorbents. V.T.Bykov, V.M.Lukyanovich, and L.V.Radushkevich 395 406

The Effect of Alternating Current on the Electrodeposition of Nickel. A.T.Vagramyan and A.A. Sutyagina 399 410

A Study of Oxygen Exchange on Vanadium Catalysts by the Use of O^{18}. L.Ya.Margolis and E.G. Plyshevskaya 403 415

Organic and Biological Chemistry

Catalytic Hydrogenation of Doubly Unsaturated Compounds Having a Conjugated System of Double Bonds. Communication 1. Hydrogenation of Bisisocrotyl. B.A.Kazansky and N.I.Popova 409 422

Page Russ page

Preparation of the Ethyl Esters of 1-(3-Bromopropyl)-2-oxocyclopentanecarboxylic Acid and of 1-(3-Chloropropyl)-2-oxocyclopentanecarboxylic Acid. N.D.Zelinsky and N.V.Elagina 419 433

Acetylene Derivatives. Communication 125. Synthesis of Polycyclic Compounds Related to the Steroids. XIII. Reaction of Carbocyclic Ketones with 1-Acetyl-1-cyclohexene. I.N.Nazarov and S.I.Zavyalov 423 437

Acetylene Derivatives. Communication 126. Synthesis of Polycyclic Compounds Related to the Steroids. XIV. Synthesis of Tetracyclic Ketones Having a Methylcyclopentane B Ring. I.N.Nazarov, V.F. Kucherov, and I.N.Terekhova 427 442

Ethylene Ester of Phosphorochloridodithious Acid, and Related Substances. A.E.Arbuzov and V.M. Zoroastrova 437 453

The Question of the Tautomerism of Isatin. A.E.Arbuzov and M.Sh.Bastanova 443 459

Synthesis and Properties of 1-Alkoxyethyl Esters of Unsaturated Carboxylic Acids ("Acylals"). M.F. Shostakovsky, N.A.Gershtein, Ya.L.Raskin, and L.E.Ostroumova 453 471

Synthesis of Sulfur Compounds by the Aid of Vinyl Ethers. Communication 5. Some New α,β'- and β,β'-Dialkoxy Derivatives of Diethyl Sulfide. E.N.Prilezhaeva, E.S.Shapiro, and M.F. Shostakovsky 459 478

Synthesis of the Vinyl Ethers of Higher Fatty Alcohols. M.F.Shostakovsky, B.I.Mikhantyev, and V.A.Neterman 465 484

Desulfurizing Action of Troshkov Kaolin. E.A.Timofeeva, N.I.Shuikin, and V.M.Klemenova 469 489

Catalytic Alkylation of Ammonia with Halogen Derivatives of Alkanes and Cycloalkanes. Communication 1. V.A.Nekrasova and N.I.Shuikin 473 495

The Preparation of Styrene by Catalytic Dehydrogenation of the Ethylcyclohexane Fraction of Maikop Gasoline. N.I.Shuikin and I.I Levitsky. 477 498

Hexadecyl Esters of Certain Inorganic Acids. B.A.Arbuzov and V.S.Vinogradova. 483 505

Viscosity and Structure of Dialkylphosphorous Acids. B.A.Arbuzov and V.S.Vinogradova. 485 507

Cyanin Dyes. Communication 1. Symmetrical N-Arylquinocyanines. G.T.Pilyugin. 491 512

Cyanin Dyes. Communication 2. Asymmetrical Carbocyanines from Derivatives of N-Arylquinaldine and of Benzothiazole. G.T.Pilyugin. 499 520

Macromolecular Compounds. Communication 44. Polyesters of Certain Aromatic Dicarboxylic Acids. V.V.Korshak and T.A.Soboleva 505 526

Macromolecular Compounds. Communication 45. Significance of the Decarboxylation of Dicarboxylic Acids in the Polycondensation Process. V.V.Korshak and S.V.Rogozhin. 509 531

The Reaction of Phosphorus Trichloride with Unsaturated Cyclic Ketones. M.I. Kabachnik and T.Ya.Medved 517 540

The Reactions of Dienic Hydrocarbons with Nitroso Compounds. Addition of 1,3-Butadiene to Nitrosobenzene. Communication 2. Yu.A.Arbuzov. 523 547

Reduction of 1-Phenylpyrrole. Yu.A.Arbuzov and M.M.Garburg 531 556

Brief Communications

Synthesis and Properties of Allylsilanes: Triallyl-α-naphthylsilane, Triallylcyclohexylsilane, Triallylbutylsilane, and Allyltributylsilane. A.D.Petrov and L.L.Shchukovskaya. 537 564

The Reactions of Dienic Hydrocarbons with Nitroso Compounds. Addition of 2,3-Dimethyl-1,3-butadiene, of 1-Phenyl-1,3-butadiene, and of Bi-1-Cyclohexen-1-yl to Aromatic Nitroso-Compounds. Yu.A.Arbuzov, N.I.Fedyukina, V.V.Shabyrina, and R.I. Shepeleva 539 566

Chronicle

	Page	Russ. page
Session of the Division of Chemical Sciences Devoted to the 125th Anniversary of the Birth of N.N. Beketov	543	570
Letter to the Editor	547	573

July-August

	Page	Russ. page
Porous Structure of Adsorbents. M.M.Dubinin	549	577
Natural Sorbents of the Far East. Communication 2. Sorption of Benzene Vapor by Natural Sorbents, and the Structure of the Sorbents. V.T.Bykov	553	583
Role of Inert Diluents in Catalytic Dehydrogenation of Ethylbenzene. N.I.Shuikin and I.I.Levitsky	559	592
Poisoning of Platinum Catalysts with a Low Content of Active Metal on a Carrier, under Conditions of Dehydrogenation Catalysis. Kh.M.Minachev, N.I.Shuikin, and I.D.Rozhdestvenskaya	567	603
Elucidation of the Role of Various Adsorptional Centers in the Reaction of Hydrogenation of Acetylene on Metallic Nickel. Communication I. Study of the Active Surface of Nickel by Means of a Differential Isotope Method. N.P.Keier	577	616
Coordination Numbers of the Ions Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} in Aqueous Solutions. O.Ya.Samoilov	585	627
Study of Systems Containing Hydrogen Peroxide. Communication 2. Thermal Properties and Dehydration of Perhydrates of Sodium Carbonate. S.Z.Makarov and V.N.Chamova	589	632
Mechanism of Reaction of Magnesium Alkyl Halides with β-Silicoalkyl Halides. A.D.Petrov and V.F.Mironov	591	635
Catalytic Alkylation of Ammonia with Halogen Derivatives of Alkanes and Cyclanes. Communication 2. Effect of the Nature of the Halogen and of Its Position in the Molecule on Amination of Alkyl Halides. V.A.Nekrasova and N.I.Shuikin	599	646
Role of Oxygen-Containing Compounds in the Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen. Yu.B.Kagan, Yu.B.Kryukov, E.V.Kamzolkina, and A.N.Bashkirov	601	649
Reactions of Diene Hydrocarbons with Nitroso Compounds. Addition of Buta-1,3-diene to p-Nitrosotoluene. Yu.A.Arbuzov	607	658
Reactions of Diene Hydrocarbons with Nitroso Compounds. Addition of Cyclohexa-1,3-diene to Nitrosobenzene. Yu.A.Arbuzov and T.A.Mastryukova	613	665
Syntheses of Acetals of Ethylene Glycol. M.F.Shostakovsky, N.A.Gershtein, and Z.S.Volkova	617	671
Synthesis and Polymerization of Vinylcaprolactam. M.F.Shostakovsky, N.A.Medzykhovskaya, and M.G.Zelenskaya	627	682
Synthesis and Transformations of Vinylcaprolactam. Communication 1. Polymerization in Presence of Hydrogen Peroxide. M.F.Shostakovsky, F.P.Sidelkovskaya, and M.G.Zelenskaya	633	690
New Synthesis of Alkyl Esters of β-Amino Acids. V.M.Rodionov and N.N.Bezinger	637	696
Acetylene Derivatives. Communication 127. Synthesis of Polycyclic Compounds Related to the Steroids. XV. Structure of the Products of Condensation of 2-Methoxybuta-1,3-diene with 1-Methylcyclohex-1-en-6-one and Methyl Methacrylate. I.N.Nazarov and S.I.Zavyalov	643	703
New Data on the Chemistry of Amides of Sulfuric Acid and Trichlorophosphazosulfonaryls. A.V.Kirsanov	649	710
New Method for Synthesis of Phosphinic and Thiophosphinic Acid Esters. Communication II. Addition of Dialkylphosphorous Acids to the Amide and Esters of Methacrylic Acid. A.N.Pudovik and D.Kh.Yarmukhametova	657	721

	Page	Russ. page
Researches in the Field of Phosphorus-Organic Compounds. Reaction of Sulfides of Phosphorus with Alcohols. M.I.Kabachnik and T.A.Mastryukova	661	727
Studies in the Field of Cyanine Dyes. Communication 3. Asymmetrical Carbocyanines from N-Arylquinaldine and Indolenine. G.T.Pilyugin	667	736
Ultra-violet Absorption Spectra of Some Derivatives of Pyridine and Nicotine. Communication 3. K.A.Zhukova, M.S.Kondakova, and Ya.L.Goldfarb	673	743
Chemical Transformations of Cellulose Macromolecules Caused by Oxidants. Communication 7. Chemical Transformation of Cellulose Due to Its Oxidation with Sodium Hypochlorite. E.D.Kaverzneva, V.I.Ivanov, and A.S.Salova	681	751
1-Ethinylcyclohexa-1,3-diene and Its Derivatives. A.D.Petrov and A.V.Kulikova	691	763
Synthesis of 1-Aryl-3-hydroxypyrrolidines. Yu.A.Arbuzov and L.I.Khmelnitsky	695	766

September-October

Esters of "Glycolphosphorous Acids". Communication 1. Compounds Having Five-, Seven-, and Eight-Membered Rings. A.E.Arbuzov and V.M.Zoroastrova	697	770
Esters of "Glycolphosphorous Acids". Communication 2. Compounds Having a Six-Membered Ring. A.E.Arubzov and V.M.Zoroastrova	705	779
N-Substituted Cyclic Esters of Phosphoramidous Acid. A.E.Arbuzov and V.M.Zoroastrova	713	789
Phosphorous Acid Derivatives Containing a Cyclohexyl Radical. A.E.Arbuzov and F.G.Valitova	723	801
Complex Compounds of Phosphorous Esters. Communication 1. Compounds with Copper, Silver, and Gold Salts. A.E.Arbuzov and V.M.Zoroastrova	729	809
Complex Compounds of Phosphorous Esters. Communication 2. Complex Compounds with Platinous Salts. A.E.Arbuzov and V.M.Zoroastrova	737	818
Complex Compounds of Phosphorous Esters. Communication 3. Complex Compounds with Mercury Salts. A.E.Arbuzov and V.M.Zoroastrova	743	826
The Tautomerism of Carbostyril Derivatives. A.E.Arbuzov and M.Sh.Bastonova	747	831
Action of Alkyl Halides on Sodium, Potassium, and Silver Dialkyl Phosphorothioates. A.E.Arbuzov and O.M.Shapshinskaya	755	842
N,N-Diethyl(dialkoxyphosphinyl)-formamides. B.A.Arbuzov and N.I.Rizpolozhensky	759	847
Esters of Ethylphosphonous Acid, and Some of Their Reactions. Communication 1. Full Esters of Ethylphosphonous Acid. B.A.Arbuzov and N.I.Rizpolozhensky	765	854
Viscosity-Structure Relationship for Phosphorous, Phosphoric, Phosphorothionic, and Boric Esters. B.A.Arbuzov and V.S.Vinogradova	773	865
Dipole Moments of N,N-Diethyl(dialkoxyphosphinyl)formamides. B.A.Arbuzov and T.G.Shavsha	781	875
Esters of Alkylphosphonic Acids, and Their Parachors. B.A.Arbuzov and V.S.Vinogradova	787	882
Certain Alkylphosphonothionic, Alkylphosphonoselenoic, Dialkylphosphinic, and Alkylphosphonous Esters, and the Mechanism of Addition to Alkylphosphonous Esters. A.I.Razumov, O.A.Mukhacheva, and Sim-Do-Khen	797	894
A New Method for the Synthesis of Phosphonic and Phosphinic Esters and Their Thio Analogs. Communication 15. Addition of Phenyl- and Alkylphosphonous Esters to Methacrylic and Acrylic Esters. A.N.Pudovik and D.Kh.Yarmukhametova	803	902

Page Russ. page

Preparation of Cyclic Acid Chlorides and Mixed Esters Derived from (Alkoxymethyl)ethylene Hydrogen Arsenites and Trimethylene Hydrogen Arsenite. Gilm Kamai and N.A.Chadaeva 807 908

"Phosphonoethylation" and Diene-Synthesis Reactions with Vinylphosphonic Esters. A.N.Pudovik and M.G.Imaev 813 916

Dechlorination of Hexachloroethane by Trialkyl Phosphites. Gilm Kamai 819 923

A New Method for the Synthesis of Phosphonic and Phosphinic Esters and Their Thio Analogs. Communication 12. Addition of Dialkylphosphorous Acids to Unsaturated Dibasic Acids and Their Esters. A.N.Pudovik 821 926

A New Method for the Synthesis of Phosphonic and Phosphinic Esters and Their Thio Analogs. Communication 13. Addition of O,O-Diethyl Hydrogen Phosphorothioite to Ketones and Aldehydes. A.N.Pudovik and G.A.Zametaeva 825 932

A New Method for the Synthesis of Phosphonic and Phosphinic Esters and Their Thio Analogs. Communication 14. New Method for the Synthesis of Amino Phosphonic Esters. A.N.Pudovik and M.V.Korchemkina 831 940

Addition of Dialkylphosphorous Acids and of Their Acid Chlorides to α-Epoxides. A.N.Pudovik and B.E.Evanov 837 947

Ethylphosphonous Esters and Some of Their Reactions. Communication 2. Partial Esters of Ethylphosphonous Acid. B.A.Arbuzov and N.I.Rizpolozhensky 843 956

The Curtius Reaction in the β-Amino Acid Series. V.M.Rodionov and N.N.Bezinger. 847 962

Organometallic "Biuret" Protein Complexes. K.T.Poroshin 855 972

Catalytic Hydrocondensation of Carbon Monoxide with Olefins. Communication 8. Hydrocondensation of Carbon Monoxide with 2-Methylpropene. Ya.T.Eidus, K.V.Puzitsky, and M.I.Batuev 859 978

Chronicle

Conference on the Trans-Effect Principle 863 982

Session in Honor of the Bicentenary of the Foundation of the Science of Physical Chemistry by M.V. Lomonosov 869 988

November-December

Toward New Successes of Soviet Chemistry. 873 993

Adsorption of Gaseous Mixtures. Communication 2. Adsorption of Ethylene and Propylene on Active Charcoal. B.P.Bering and V.V.Serpinsky 877 997

Studies of Capillary Condensation of Vapors in Highly Disperse Systems. Communication 1. Calculation of Capillary Condensation in the Vicinity of Points of Contact of Spherical Particles. L.V.Radushkevich 885 1008

Catalytic Oxidation of Phosphine over a Wide Range of Temperatures. E.A.Andreev and N.N.Kavtaradze 895 1021

Electron Absorption Spectra of Polystyrene and Its Derivatives. M.V.Volkenshtein and N.S.Kolodina . . . 903 1033

Preparation of Trichloroalkoxytitanes from Titanium Tetrachloride and Alcohols. A.N.Nesmeyanov, R.Kh.Freidlina, and O.V.Nogina 907 1037

Synthesis of Aromatic Arsenic-Organic Compounds Through Arylazocarboxylic Salts. O.A.Reutov and Yu.G.Bundel 911 1041

New Data on the Chemistry of Pyrazolone Derivatives. V.M.Rodionov and A.M.Fedorova. 917 1049

Acetylene Derivatives. 128. Heterocyclic Compounds. XXIII. Action of Primary Aromatic Amines

Page Russ. page

and α-Aminopyridine on Vinyl Allyl Ketones. Synthesis of Aryl-Substituted γ-Piperidones and 1-(α-Pyridyl)-4-piperidones. I.N.Nazarov, S.G.Matsoyan, and V.A.Rudenko 923 1057

Acetylene Derivatives. 129. Heterocyclic Compounds. XXIV. Transformations of 1-Phenyl-2,5-dimethyl-4-piperidone. I.N.Nazarov, S.G.Matsoyan, and V.A.Rudenko 933 1069

Catalytic Hydrocondensation of Carbon Monoxide with Olefins. Communication 9. Reaction of Methanol and Ethanol with Ethylene. Ya.T.Eidus and I.V.Guseva 939 1075

Synthesis and Properties of Tetrapropylmethane, Tetrabutylmethane, and Tetrahexylsilane. A.D. Petrov and E.A.Chernyshev 945 1082

Behavior of γ-Halogenodialkenyls in the Grignard-Wurtz Synthesis. A.D.Petrov, M.A.Cheltsova, and E.A.Chernyshev 949 1087

Researches on Acetylenic Alcohols and Glycols. Communication 2. Synthesis of Mono- and Di-Acetals of Tetramethylbutindiol. M.F.Shostakovsky and A.V.Bogdanova 955 1094

Indirect Vinylation of Aliphatic Alcohols. M.F.Shostakovsky, B.I.Mikhantyev, and N.N.Ovchinnikova. 959 1099

Metallo-Organic "Biuret" Complexes of Protein Breakdown Products. K.T.Poroshin 963 1105

High-Molecular Compounds. Communication 52. Reactions of Polyester Macromolecules with Each Other. V.V.Korshak and S.V.Vinogradova 967 1109

Remarks on "The Theory of Resonance or Mesomerism". Ya.K. Syrkin and M.E.Dyatkina 973 1116

Free Energy and Heat of Dehydration of Crystal-Hydrates of Uranyl Nitrate and Chloride. A.F.Kapustinsky and L.I.Baranova 981 1122

Synthesis of Silicohydrocarbons from β-Silicohalides and Alkyl-Lithium. A.D.Petrov and V.P. Lavrishchev 985 1125

Synthesis and Properties of Unsaturated Silicohydrocarbons: Dimethyldi-(methylallyl)-silane, Methyldi(methylallyl)-silane, Methyltri-(methylallyl)-silane, Tetra-(methylallyl)-silane, Trimethylcyclopentadienylsilane, and Trimethylbut-3-enylsilane. A.D.Petrov and G.I.Nikishin. 989 1128

Structure and Certain Properties of Dibenzhydrylthiophen. Ya.L.Goldfarb and M.S.Kondakova 993 1131

Chronicle

Conference on the Chemistry and Physical Chemistry of High-Molecular Compounds 997 1134

General Meeting of the Division of Chemical Sciences of the Academy of Sciences, USSR, to Celebrate the 75th Birthday of Academician A.E.Arbuzov 1003 1138

Meeting of the Commission for the Editing of D.I.Mendeleev's Scientific Legacy and the Publication of His Works 1005 1139

AUTHOR INDEX, 1952

Ageev, N.V., and L.N.Guseva. Experimental study of the electron density in crystals. 5. Electron density of Mg_2Si, 31.

Akimov, G.V., see Gurvich, L.Ya.

Andreev, E.A., and N.N.Kavtaradze. Catalytic oxidation of phosphine over a wide range of temperatures, 895.

Arbuzov, A.E. Ninety years of A.M.Butlerov's theory of chemical structure, 1.

Arbuzov, A.E., and M.Sh. Bastanova. The question of the tautomerism of isatin, 443.

Arbuzov, A.E., and M.Sh. Bastonova. The tautomerism of carbostyril derivatives, 747.

Arbuzov, A.E., and O.M.Shapshinskaya. Action of alkyl halides on sodium, potassium, and silver dialkylphosphorothioates, 755.

Arbuzov, A.E., and F.G.Valitova. Phosphorous acid derivatives containing a cyclohexyl radical, 723.

Arbuzov, A.E., and V.M.Zoroastrova. Complex compounds of phosphorous esters. 1. Compounds with copper, silver, and gold salts, 729.

Arbuzov, A.E., and V.M.Zoroastrova. Complex compounds of phosphorous esters. 2. Complex compounds with platinous salts, 737.

Arbuzov, A.E., and V.M.Zoroastrova. Complex compounds of phosphorous esters. 3. Complex compounds with mercury salts, 743.

Arbuzov, A.E., and V.M.Zoroastrova. Esters of "glycolphosphorous acids". 1. Compounds having five-, seven-, and eight-membered rings, 697.

Arbuzov, A.E., and V.M.Zoroastrova. Esters of "glycolphosphorous acids". 2. Compounds having a six-membered ring, 705.

Arbuzov, A.E., and V.M.Zoroastrova. Ethylene ester of phosphorochloridodithious acid, and related substances, 437.

Arbuzov, A.E., and V.M.Zoroastrova. N-Substituted cyclic esters of phosphoramidous acids, 713.

Arbuzov, B.A. The development of organic chemistry in the light of A.M.Butlerov's teaching, 13.

Arbuzov, B.A., and N.P.Grechkin. Synthesis of 7-benz[a]anthracenemethanephosphonic and 12-methyl-7-benz[a]anthracenemethanephosphonic acids, 131.

Arbuzov, B.A., and N.I.Rizpolozhensky. N,N-Diethyl(dialkoxyphosphinyl)formamides, 759.

Arbuzov, B.A., and N.I.Rizpolozhensky. Ethylphosphonous esters and some of their reactions. 2. Partial esters of ethylphosphonous acid, 843.

Arbuzov, B.A., and T.G.Shavsha. Dipole moments of N,N-diethyl(dialkoxyphosphinyl)formamides, 781.

Arbuzov, B.A., and N.I.Rizpolozhensky. Esters of ethylphosphonous acid, and some of their reactions. 1. Full esters of ethylphosphonous acid, 765.

Arbuzov, B.A., and V.S.Vinogradova. Hexadecyl esters of certain inorganic acids, 483.

Arbuzov, B.A., and V.S.Vinogradova. Viscosity and structure of dialkylphosphorous acids, 485.

Arbuzov, B.A., and V.S.Vinogradova. Viscosity-structure relationship for phosphorous, phosphoric, phosphorothionic, and boric esters, 773.

Arbuzov, B.A., and V.S.Vinogradova. Esters of alkylphosphonic acids, and their parachors, 787.

Arbuzov, Yu. A. Reactions of diene hydrocarbons with nitroso compounds 1. Addition of buta-1,3-diene to p-nitrosobenzene, 339.

Arbuzov, Yu.A. Reactions of diene hydrocarbons with nitroso compounds. 2. Addition of 1,3-butadiene to nitrosobenzene, 523.

Arbuzov, Yu.A. Reactions of diene hydrocarbons with nitroso compounds. 3. Addition of buta-1,3-diene to p-nitrosotoluene, 607.

Arbuzov, Yu.A., N.L.Fedyukina, V.V.Shabyrina and R.I.Shepeleva. The reactions of diene hydrocarbons with nitroso compounds. Addition of 2,3-dimethyl-1,3-butadiene, of 1-phenyl-1,3-butadiene, and of bi-1-cyclohexen-1-yl to aromatic nitroso compounds, 539.

Arbuzov, Yu.A., and M.M. Garburg. Reduction of 1-phenylpyrrole, 531.

Arbuzov, Yu.A., and L.I.Khmelnitsky. Synthesis of 1-aryl-3-hydroxypyrrolidines, 695.

Arbuzov, Yu.A., and A.Markovskaya. Reactions of diene hydrocarbons with nitroso compounds. Reaction of buta-1,3-diene, 2,3-dimethylbuta-1,3-diene, and cyclohexa-1,3-diene with 1-chloro-1-nitrosocyclohexane, 355.

Arbuzov, Yu.A., and T.A.Mastryukova. Reactions of diene hydrocarbons with nitroso compounds. Addition of cyclohexa-1,3-diene to nitrosobenzene, 613.

Baranova, L.I., see Kapustinsky, A.F.

Baron, V.V., see Savitsky, E.M.

Bashkirov, A.N., see Kagan, Yu.B.

Bastonova, M.Sh., see Arbuzov, A.E.

Batuev, M.I., see Eidus, Ya. T.

Bazhenov, N.M., and M.V.Volkenshtein. Optical activity of cellulose triacetate, 333.

Bering, B.P., and V.V.Serpinsky. Adsorption of gaseous mixtures. 2. Adsorption of ethylene and propylene on active charcoal, 877.

Bezinger, N.N., see Rodionov, V.M.

Bogdanova, A.V., see Shostakovsky, M.F.

Bundel, Yu.G., see Reutov, O.A.

Bykov, G.V. Distribution of π-electron density and interatomic distances. 2. 359.
Bykov, V.T. Natural sorbents of the Far East. 2. Sorption of benzene vapor by natural sorbents, and the structure of sorbents, 553.
Bykov, V.T., V.M.Lukyanovich, and L.V.Radushkevich. Natural sorbents of the Far East. 1. Electron-microscope investigations of natural sorbents, 395.

Chadaeva, N.A., see Kamai, Gilm.
Chamova, V.N., see Makarov, S.Z.
Chekulaeva, I.A., see Shostakovsky, M.P.
Chelintsev, G.V. Answer to the critics of the new structural theory, 205.
Cheltsova, M.A., see Petrov, A.D.
Chernyshev, E.A., see Petrov, A.D.

Dubinin, M.M. Porous structure of adsorbents, 549.
Dyatkina, M.E., see Syrkin, Ya.K.

Eidus, Ya. T., and I.V.Guseva. Catalytic hydrocondensation of carbon monoxide with olefins. 9. Reaction of methanol and ethanol with ethylene, 939.
Eidus, Ya.T., K.V.Puzitsky, and N.I.Ershov. Catalytic hydrocondensation of carbon monoxide with olefins. 7. Effect of the carbon monoxide concentration on the hydrocondensation reactions of carbon monoxide with propene and with n-butene, 157.
Eidus, Ya. T., K.V.Puzitsky, and M.I.Batuev. Catalytic hydrocondensation of carbon monoxide with olefins. 8. Hydrocondensation of carbon monoxide with 2-methylpropene, 859.
Elagina, N.V., see Zelinsky, N.D.
Ershov, N.I., See Eidus, Ya. T.

Fedorov, B.P., and N.V.Ptitsina. Investigation of anthracene derivatives. 10. The relative activities of the meso carbon atom of anthracene and 9,10-dichloroanthracene in reactions with oxidizing agents, 135.
Fedorova, A.M., see Rodionov, V.M.
Fedyukina, N.L., see Arbuzov, Yu.A.
Feofanova, L.M., see Shuikin, N.I.
Fokin, A.V., see Knunyants, I.L.
Freidlina, R.Kh. Letter to the editor, on "Theory of Resonance", 547.
Freidlina, R.Kh., see Nesmeyanov, A.N.
Freidlina, R.Kh., see Nogina, O.V.
Freydlin, L.Kh, and A.M.Levit. Kinetics of the dehydration of alcohols in presence of tricalcium phosphate, 177.

Garburg, M.M., see Arbuzov, Yu.A.
Gavrilov, A.E., see Gonikberg, M.G.
Gershtein, N.A., see Shostakovsky, M.F.
Goldfarb, Ya. L., and M.S.Kondakova. Structure and certain properties of dibenzhydrylthiophen, 993.
Goldfarb, Ya. L., see Zhukova, K.A.
Gonikberg, M.G., A.E.Gavrilov, and B.A.Kazansky. Isomerization of alkanes in presence of $AlCl_3$ under pressure of hydrogen. 1. Isomerization of n-hexane, 171.
Grechkin, N.P., see Arbuzov, B.A.
Grinberg, A.A., and K.B.Yatsimirsky. Periodic law of D.I. Mendeleev and the stability of coordination compounds, 239.
Gurvich, L.Ya., and G.V.Akimov. Electrochemical behavior of iron in oxidizing media. 3. Cathodic polarization of iron in oxidizing media, 377.
Guseva, L.N., see Ageev, N.V.
Guseva, I.V., see Eidus, Ya. T.

Imaev, M.G., see Pudovik, A.N.
Ivanov, B.E., see Pudovik, A.N.
Ivanov, V.I., see Kaverzneva, E.D.

Kabachnik, M.I., and T.A.Mastryukova. Researches in the field of phosphorus-organic compounds. Reaction of sulfides of phosphorus with alcohols, 661.
Kabachnik, M.I., and T.Ya.Medved. The reaction of phosphorus trichloride with unsaturated cyclic ketones, 517.
Kagan, Yu.B., Yu.B.Kryukov, E.V.Kamzolkina, and A.N. Bashkirov. Role of oxygen-containing compounds in the synthesis of hydrocarbons from carbon monoxide and hydrogen, 601.
Kamai, Gilm, Dechlorination of hexachlorethane by trialkylphosphites, 819.
Kamai, Gilm, and N. A. Chadaeva. Preparation of cyclic acid chlorides and mixed esters derived from (alkoxymethyl)ethylene hydrogen arsenites and trimethylene hydrogen arsenite, 807.
Kamzolkina, E.V., see Kagan, Yu.B.
Kapustinsky, A.F., and L.I.Baranova. Free energy and heat of dehydration of crystal hydrates of uranyl nitrate and chloride, 981.
Kapustinsky, A.F., and O.Ya. Samoilov. Thermochemistry and structure of atoms. 6. Thermochemistry of boron. Application of the rule of thermochemical logarithmics to elements of the third group of D.I. Mendeleev's system, 245.
Kaverzneva, E.D., V.I.Ivanov, and A.S.Salova. Chemical changes produced in the cellulose macromolecule by oxidizing agents. 6. The presence in oxycelluloses

of carbonic ester groupings and their effect on the estimation of uronic carboxyl groups, 199.

Kaverzneva, E.D., V.I.Ivanov, and A.S.Salova. Chemical transformations of cellulose macromolecules caused by oxidizing agents. 7. Chemical transformations of cellulose due to its oxidation with sodium hypochlorite, 681.

Kavtaradze, N.N., see Andreev, E.A.

Kazansky, B.A., see Gonikberg, M.G.

Kazansky, B.A. and M.Yu.Lukina. Synthesis of hydrocarbons of the cyclobutane series. 2. 1-Methyl-3-ethylcyclobutane and di-(3-methylcyclobutyl)methane, 319.

Kazansky, B.A., and N.I.Popova. Catalytic hydrogenation of doubly unsaturated compounds having a conjugated system of double bonds. 1. Hydrogenation of biisocrotyl, 409.

Keier, N.P. Elucidation of the role of various adsorptional centers in the reaction of hydrogenation of acetylene on metallic nickel. Study of the active surface of nickel by means of a differential isotope method, 577.

Khmelnitsky, L.L., see Arbuzov, Yu.A.

Kirsanov, A.V. New data on the chemistry of amides of sulfuric acid and trichlorophosphazosulfonaryls, 649.

Kiseleva, T.S., see Rodionov, V.M.

Kleimenova, V.M., see Timofeeva, E.A.

Knunyants, I.L., and A.V.Fokin. Addition reactions of perfluoro olefins, 279.

Kochetkov, N.K., A.N.Nesmeyanov, and N.A.Semenov. Synthesis of isoxazoles from β-chlorovinyl ketones, 97.

Kolodina, N.S., see Volkenshtein, M.V.

Kondakova, M.S., see Goldfarb, Ya. L.

Kondakova, M.S., see Zhukova, K.A.

Korchemkina, M.V., see Pudovik, A.N.

Korshak, V.V., and S.V.Rogozhin. Macromolecular compounds 45. Significance of the decarboxylation of dicarboxylic acids in the polycondensation process, 509.

Korshak, V.V., and T.A.Soboleva. Macromolecular compounds. 44. Polyesters of certain aromatic dicarboxylic acids, 505.

Korshak, V.V., and S.V.Vinogradova. High-molecular compounds. 52. Reactions of polyester macromolecules with each other, 967.

Korshak, V.V., and S.V.Vinogradova. Macromolecular compounds. 43. Significance of acidolysis in the polyesterification reaction, 193.

Kovalskaya, M.P., see Nikitin, B.A.

Kryukov, Yu.B., see Kagan, Yu.B.

Kucherov, V.F., see Nazarov, I.N.

Kulikova, A.V., see Petrov, A.D.

Kurtev, B.I., see Rodionov, V.M.

Lavrishchev, V.P., see Petrov, A.D.

Levit, A.M., see Freydlin, L.Kh.

Levitsky, I.I., see Shuikin, N.I.

Lukina, M.Yu., see Kazansky, B.A.

Lukyanovich, V.M., see Bykov, V.T.

Lyashenko, V.S. Thermodynamic study of the systems cadmium — zinc, cadmium — lead, cadmium — tin, bismuth — cadmium, tin — zinc, and lead — tin, 255.

Makarov, S.Z., and V.N.Chamova. Study of systems containing hydrogen peroxide. 2. Thermal properties of dehydration of perhydrates of sodium carbonate, 589.

Margolis, L.Ya., and E.G.Plyshevskaya. A study of oxygen exchange on vanadium catalysts by the use of O^{18}, 403.

Margolis, L.Ya., and O.M.Todes. Catalytic oxidation of ethylene on magnesium chromite, 55.

Markovskaya, A., see Arbuzov, Yu.A.

Mastryukova, T.A., see Kabachnik, M.I.

Matsoyan, S.G., see Nazarov, I.N.

Medved, T.Ya., see Kabachnik, M.I.

Medzykovskaya, N.A., see Shostakovsky, M.F.

Meshcheryakov, A.P., and L.V.Petrova. The splitting-off of the elements of hydrogen halide from monohalo derivatives of hydrocarbons of the series C_nH_{2n+2}, 165.

Mikhantyev, B.I., see Shostakovsky, M.F.

Minachev, Kh.M., N.I.Shuikin, and I.D.Rozhdestvenskaya. Poisoning of platinum catalysts with a low content of active metal on a carrier under conditions of dehydrogenation catalysis, 567.

Mironov, V.F., see Petrov, A.D.

Mukhacheva, O.A., see Razumov, A.I.

Nazarov, I.N., and V.F.Kucherov. Synthesis of polycyclic compounds related to the steroids. XI. Researches on the stereochemistry of cyclic compounds. I. Condensation of divinyl with citraconic and mesaconic acid and their esters. Cis-trans isomerism of 1-methylcyclohexane-1,2,dicarboxylic acids and their esters, 301.

Nazarov, I.N., S.G.Matsoyan, and V.A.Rudenko. Acetylene derivatives, 128. Heterocyclic compounds. XXIII. Action of primary aromatic amines and α-aminopyridine on vinyl allyl ketones. Synthesis of aryl-substituted γ-piperidones and 1-(α-pyridyl)-4-piperidones, 923.

Nazarov, I.N., S.G.Matsoyan, and V.A.Rudenko. Acetylene derivatives. 129. Heterocyclic compounds. XXIV. Transformations of 1-phenyl-2,5-dimethyl-4-piperidone, 933.

Nazarov, I.N., V.F.Kucherov, and L.N.Terekhova. Acetylene derivatives. 126. Synthesis of polycyclic compounds related to the steroids. XIV. Synthesis of tetracyclic ketones having a methylcyclopentane B ring, 427.

Nazarov, I.N., and S.I.Zavyalov. Synthesis of steroid compounds and related substances. XII. Condensation of cyclic β-diketones with vinyl ketones, and transformations of the resulting products, 309.

Nazarov, I.N., and S.I.Zavyalov. Synthesis of polycyclic compounds related to the steroids. XIII. Reaction of carbocyclic ketones with 1-acetyl-1-cyclohexene, 423.

Nazarov, I.N., and S.I.Zavylov. Acetylene derivatives. 127. Synthesis of polycyclic compounds related to the steroids. XV. Structure of the products of condensation of 2-methoxybuta-1,3-diene with 1-methylcyclohex-1-en-6-one and methyl methacrylate, 643.

Nekrasova, V.A., and N.I.Shuikin. Catalytic alkylation of ammonia with halogen derivatives of alkanes and cycloalkanes. 1. 473.

Nekrasova, V.A., and N.I.Shuikin. Catalytic alkylation of ammonia with halogen derivatives of alkanes and cyclanes. 2. Effect of the nature of the halogen and of its position in the molecule on amination of alkyl halides, 599.

Nesmeyanov, A.N. "Contact Bonds" and the "New Structural Theory", 215.

Nesmeyanov, A.N., R.Kh. Freidlina, and O.V.Nogina. Preparation of trichloroalkoxytitanes from titanium tetrachloride and alcohols, 907.

Nesmeyanov, A.N., B.A.Sazonova, and E.I.Vasilyeva. Stereoisomeric sodium enolates, 87.

Nesmeyanov, A.N., see Kochetkov, N.K.

Nesmeyanov, A.N., see Nogina, O.V.

Neterman, V.A., see Shostakovsky, M.F.

Nikishin, G.I., see Petrov, A.D.

Nikitin, B.A., and M.P.Kovalskaya. Phenol compounds of the inert gases and their analogs, 23.

Nogina, O.V., R.Kh. Freidlina, and A.N.Nesmeyanov. New method of synthesizing trialkoxytitanium chlorides, 81.

Nogina, O.V., see Nesmeyanov, A.N.

Ostroumova, L. E., see Shostakovsky, M. F.

Ovchinnikova, N. N., see Shostakovsky, M. F.

Petrov, A.D., M.A.Cheltsova, and E.A.Chernyshev. Behavior of γ-halogenodialkenyls in the Grignard-Würtz synthesis, 949.

Petrov, A.D., and E.A.Chernyshev. Synthesis and properties of tetrapropylmethane, tetrabutylmethane, and tetrahexylsilane, 945.

Petrov, A.D., and A.V.Kulikova. 1-Ethinylcyclohexa-1,3-diene and its derivatives, 691.

Petrov, A.D., and V.P.Lavrishchev. Synthesis of silicohydrocarbons from β-silicohalides and alkyl-lithium, 985.

Petrov, A.D., and V.F.Mironov. Mechanism of reaction of magnesium alkyl halides with β-silicoalkyl halides, 591.

Petrov, A.D., and G.I.Nikishin. Synthesis and properties of unsaturated silicohydrocarbons: dimethyldi(methylallyl)silane, methyldi-(methylallyl)-silane, methyltri-(methylallyl)silane, tetra-(methylallyl)silane, trimethylcyclopentadienylsilane, and trimethylbut-3-enylsilane, 989.

Petrov, A.D., and L.L.Shchukovskaya. Synthesis and properties of allylsilanes: triallyl-α-naphthylsilane, triallylbutylsilane, and allyltributylsilane, 537.

Petrov, D.A., and L.A.Raikovskaya. Microhardness method of studying intracrystalline liquation. 1. Nature of the phenomenon of intracrystalline liquation, 251.

Petrova, L.V., see Meshcheryakov, A.P.

Pilyugin, G.T., Cyanine dyes. 1. Symmetrical N-arylquinocyanines, 491.

Pilyugin, G.T. Cyanine dyes. 2. Asymmetrical carbocyanines from derivatives of N-arylquinaldine and of benzothiazole, 499.

Pilyugin, G.T. Cyanine dyes. 3. Asymmetrical carbocyanines from N-arylquinaldine and indolenine, 667.

Pilyugin, G.T. Studies of quinoline derivatives. I. N-Aryl quaternary salts of quinoline derivatives, 347.

Plyshevskaya, E.G., see Margolis, L.Ya.

Popova, N.I., see Kazansky, B.A.

Poroshin, K.T. Metallo-organic "Biuret" complexes of protein breakdown products, 963.

Poroshin, K.T. Organometallic "Biuret" protein complexes, 855.

Pribytkova, N.A., see Rubinshtein, A.M.

Prilezhaeva, E.N., E.S.Shapiro, and M.F.Shostakovsky. Synthesis of sulfur compounds by the aid of vinyl ethers. 5. Some new α,β- and β,β'-dialkoxyderivatives of diethyl sulfides, 459.

Ptitsina, N.V., see Fedorov, B.P.

Ptitsyna, O.A., see Reutov, O.A.

Pudovik, A.N. New method for the synthesis of phosphonic and phosphinic esters and their thio analogs. 12. Addition of dialkylphosphorous acids to unsaturated dibasic acids and their esters, 821.

Pudovik, A.N., and B.E.Ivanov. Addition of dialkylphosphorous acids and of their acid chlorides to α-epoxides, 837.

Pudovik, A.N., and M.G.Imaev. "Phosphonoethylation" and diene-synthesis reactions with vinylphosphonic esters, 813.

Pudovik, A.N., and M.V.Korchemkina. New method for the synthesis of phosphonic and phosphinic esters and their thio analogs. 14. New method for the synthesis of amino phosphonic esters, 831.

Pudovik, A.N., and D.Kh. Yarmukhametova. New method for synthesis of phosphinic acid esters. 11. Addition of dialkylphosphorous acids to the amide

and esters of methacrylic acid, 657.
Pudovik, A.N., and D.Kh. Yarmukhametova. New method for the synthesis of phosphonic and phosphinic esters and their thio analogs. 15. Addition of phenyl- and alkyl- phosphonous esters to methacrylic and acrylic esters, 803.
Pudovik, A.N., and G.A.Zametaeva. New method for the synthesis of phosphonic and phosphinic esters and their thio analogs. 13. Addition of O, O-diethyl hydrogen phosphorothioite to ketones and aldehydes, 825.
Puzitsky, K.V., see Eidus, Ya. T.

Radushkevich, L.V. Studies of capillary condensation of vapors in highly disperse systems. 1. Calculation of capillary condensation in the vicinity of points of contact of spherical particles, 885.
Radushkevich, L.V., see Bykov, V.T.
Raikovskaya, L.A., see Petrov, D.A.
Raskin, Ya. L., see Shostakovsky, M.F.
Razumov, A.I., O.A.Mukhacheva, and Sim-Do-Khen. Certain alkylphosphonothionic, alkylphosphonoselenonic, dialkylphosphinic, and alkylphosphonous esters, and the mechanism of addition to alkylphosphonous esters, 797.
Reutov, O.A., and Yu.G.Bundel. Synthesis of aromatic arsenic-organic compounds through arylazocarboxylic salts, 911.
Reutov, O.A., and O.A.Ptitsyna. Synthesis of aromatic organo-antimony compounds by the aid of arylazoformates, 103.
Rizpolozhensky, N.I., see Arbuzov, B.A.
Rodionov, V.M., and N.N.Bezinger. New synthesis of alkyl esters of β-amino acids, 637.
Rodionov, V.M., and N.N.Bezinger. The Curtius reaction in the β-amino acid series, 847.
Rodionov, V.M., and A.M.Fedorova. New data on the chemistry of pyrazolone derivatives, 917.
Rodionov, V.M., and T.S.Kiseleva. Synthesis of β-amino-β-cyclohexylpropionic acid and some of its derivatives, 293.
Rodionov, V.M., and B.I.Kurtev. Synthesis and characterization of β-(β-naphthyl)-β-aminopropionic acid and certain of its derivatives. 1. 123.
Rodionov, V.M., and B.I.Kurtev. 2-(2'-Naphthyl)-2-aminopropionic acid and its pyrimidine derivatives, 2. 285.
Rodionov, V.M., and N.G.Yartseva. Investigations relating to β-amino acids. Synthesis and reactions of β-aminobutyric acid, 113.
Roginsky, S.Z. and M.I.Yanovsky The theory of chromatography on heterogeneous surfaces. 1. Determination from desorption curves of the function expressing the distribution with respect to their heats of adsorption of sites on a solid surface, 63.
Roginsky, S.Z., and M.I.Yanovsky. The theory of chromatography on heterogeneous surfaces. 3. Dynamics of the adsorption of mixtures on heterogeneous surfaces, 69.
Rogozhin, S.V., see Korshak, V.V.
Rozhdestvenskaya, I.D., see Minachev, Kh. M.
Rubinshtein, A.M., V.E.Vasserberg, and N.A.Pribytkova. Effect of the dimensions of the elementary crystallites on the porosity and activity of Al_2O_3 catalysts of dehydration reactions, 325.
Rudenko, V.A., see Nazarov, I.N.

Salova, A.S., see Kaverzneva, E.D.
Samoilov, O.Ya. Coordination numbers and hydration of the ions Li^+, Na^+, K^+, Cl^-, Br^-, and I^- in aqueous solutions, 389.
Samoilov, O.Ya. Coordination numbers of the ions Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} in aqueous solutions, 585.
Samoilov, O.Ya., see Kapustinsky, A.F.
Savitsky, E.M., and V.V.Baron. Mechanical properties of alloys of the magnesium—cadmium system, 383.
Sazonova, B.A., see Nesmeyanov, A.N.
Semeonov, N.A., see Kochetkov, N.K.
Serpinsky, V.V., see Bering, B.P.
Shabyrina, V.V., see Arbuzov, Yu.A
Shantarovich, P.S. Kinetics of the polymerization of compounds containing a conjugated link. Polymerization of methyl acrylate, 41.
Shantarovich, P.S. Kinetics of polymerization of compounds with conjugated double bonds. Polymerization of methyl acrylate in absence of light. 265.
Shapiro, E.S., see Prilezhaeva, E.N.
Shapshinskaya, O.M., see Arbuzov, A.E.
Shavsha, T.G., see Arbuzov, B.A.
Shchukovskaya, L. L., see Petrov, A.D.
Shepeleva, R.I., see Arbuzov, Yu. A.
Shostakovsky, M.F., and A.V.Bogdanova. Researches on acetylenic alcohols and glycols. 2. Synthesis of mono- and diacetals of tetramethylbutindiol, 955.
Shostakovsky, M.F., I.A.Chekulaeva, and N.A.Gershtein. The synthesis and reactions of vinyl ethers of ethanolamines. 2. The synthesis of aminoacetals, 185.
Shostakovsky, M.F., N.A.Gershtein, and Z.S.Volkova. Synthesis of acetals of ethylene glycol, 617.
Shostakovsky, M.F., B.I.Mikhantyev, and V.A.Neterman. Synthesis of the vinyl ethers of higher fatty alcohols. 465.
Shostakovsky, M.F., B.I.Mikhantyev, and N.N.Ovchinni-

kova. Indirect vinylation of aliphatic alcohols. 959.
Shostakovsky, M.F., N.A.Gershtein, Ya.L.Raskin, and L.E.Ostroumova. Synthesis and properties of α-alkoxyethyl esters of unsaturated carboxylic acids ("acylals"). 453.
Shostakovsky, M.F., N.A.Medzykovskaya, and M.G. Zelenskaya. Synthesis and polymerization of vinylcaprolactam, 627.
Shostakovsky, M.F., F.P.Sidelkovskaya, and M.G. Zelenskaya. Synthesis and transformations of vinylcaprolactam. 1. Polymerization in presence of hydrogen peroxide, 633.
Shostakovsky, M.F., see Prilezhaeva, E.N.
Shuikin, N.I., and L.M.Feofanova. Reactions of methylcyclohexane and toluene in contact with aluminum chloride, 149.
Shuikin, N.I., and I.I.Levitsky. The preparation of styrene by catalytic dehydrogenation of the ethylcyclohexane fraction of Maikop gasoline, 477.
Shuikin, N.I., and I.I.Levitsky. Role of inert diluents on catalytic dehydrogenation of ethylbenzene, 559.
Shuikin, N.I., see Minachev, Kh.M.
Shuikin, N.I., see Nekrasova, V.A.
Shuikin, N.I., see Timofeeva, E.A.
Sidelkovskaya, F.P., see Shostakovsky, M.F.
Sim-Do-Khen, see Razumov, A.I.
Soboleva, T.A., see Korshak, V.V.
Sutyagina, A.A., see Vagramyan, A.T.
Sveshnikova, V.N. Investigation of solubility in the reciprocal system $CaSO_4 - KCl - H_2O$ at 55°, 45.
Syrkin, Ya. K., and M.E.Dyatkina. Remarks on "The theory of resonance or mesomerism", 973.

Terekhova, L.N., see Nazarov, I.N.
Timofeeva, E.A., N.I.Shuikin, and V.M.Kleimenova. Desulfurizing action of Troshkov kaolin, 469.
Todes, O.M., see Margolis, L.Ya.

Vagramyan, A.T., and A.A. Sutyagina. The effect of alternating current on the electrodeposition of nickel, 399.
Valitova, G.F., see Arbuzov, A.E.
Vasilyeva, E.I., see Nesmeyanov, A.N.
Vasserberg, V.E., see Rubinshtein, A.M.
Vinogradova, V.S., see Arbuzov, B.A.
Vinogradova, S.V., see Korshak, V.V.
Volkenshtein, M.V., and N.S.Kolodina. Electron absorption spectra of polystyrene and its derivatives, 903.
Volkenshtein, M.V., see Bazhenov, N.M.
Volkova, Z.S., see Shostakovsky, M.F.
Volshtein, L.M. A new class of coordination compounds of chromium with amino acids, 269.

Yanovsky, M.I., see Roginsky, S.Z.
Yarmukhametova, D.Kh., see Pudovik, A.N.
Yartseva, N.G., see Rodionov, V.M.
Yatsimirsky, K.B., see Grinberg, A.A.

Zametaeva, G.A., see Pudovik, A.N.
Zavyalov, S.I., see Nazarov, I.N.
Zelenskaya, M.G., see Shostakovsky, M.F.
Zelinsky, N.D., and N.V.Elagina. The preparation of the ethyl esters of 1-(3-bromopropyl)-2-oxocyclopentanecarboxylic acid, and of 1-(3-chloropropyl)-2-oxocyclopentanecarboxylic acid, 419.
Zelinsky, N.D., see Eidus, Ya. T.
Zhukova, K.A., M.S.Kondakova, and Ya.L.Goldfarb. Ultraviolet absorption spectra of some derivatives of pyridine and nicotine. 3. 673.
Zoroastrova, V. M., see Arbuzov, A. E.

Absorption spectra, of copper, "biuret" organometallic protein complexes, 855.
— of copper "biuret" complexes of protein breakdown products, 963.
— electron, of polystyrene and its derivatives, 903.
— ultra-violet, of some derivatives of pyridine and nicotine, 673.
Acetals, amino, synthesis, 185.
— alkyl phenyl, preparation, properties, hydrolysis, 959.
— dialkyl, synthesis, 617.
— of ethylene glycol, syntheses of, 617.
— β-hydroxyethylalkyl, preparation, 617.
— mono- and di-, of tetramethylbutindiol, synthesis of, 955.
1-Acetyl-1-cyclohexene, reaction of carbocyclic ketones with, 423.
Acetylene, hydrogenation of, on metallic nickel, elucidation of the role of various adsorptional centers, 577.
Acetylene derivatives. Communication 126. Synthesis of polycyclic compounds related to steroids. Synthesis of tetracyclic ketones having a methylcyclopentane B ring, 427.
— Communication 127. Synthesis of polycyclic compounds related to the steroids. Structure of the products of condensation of 2-methoxybuta-1,3-diene with 1-methylcyclohex-1-en-6-one and methyl methacrylate, 643.
— Com. 128. Heterocyclic compounds. Action of primary aromatic amines and α-aminopyridine on vinyl allyl ketones. Synthesis of aryl-substituted γ-piperidones and 1-(α-pyridyl)-4-piperidones, 923.
— Com. 129. Heterocyclic compounds. Transformations of 1-phenyl-2,5-dimethyl-4-piperidone, 933.
Acetylenic alcohols, preparation of, 691.
Acetylenic alcohols and glycols, researches on, 955.
Acetylenic glycols, researches on, 955.
Acid, adipic, kinetics, of acidolysis of ethyl stearate with, 193.
Acid, β-aminobutyric, synthesis and reactions of, 113.
Acid, β-amino-β-cyclohexylpropionic, and some of its derivatives, synthesis of, 293.
Acid, ethylphosphonous, esters of, and some of their reactions, 765.
— partial esters of, 843.
Acid, methacrylic, addition of dialkylphosphorous acids to the amide and esters of, 657.
Acid, β-(β-naphthyl)-β-aminopropionic, and certain of its derivatives, synthesis and characterization of, 123.
Acid, 2-(2'-naphthyl)-2-aminopropionic, and its pyrimidine derivatives. 285.
Acid, phosphoramidous, N-substituted cyclic esters of, 713.
— phosphorochloridodithious, ethylene ester of, and related substances, 437.
— phosphorochloridous, cyclic esters of, preparation, 705; preparation of cyclic esters of, 697.
— phosphorous, derivatives of, containing a cyclohexyl radical, 723.
— succinic, kinetics of acidolysis of ethyl stearate with, 193.
— chlorides, of dialkylphosphorous acids, addition to α-epoxides, 837.
— chlorides, cyclic, and mixed esters derived from (alkoxymethyl)ethylene hydrogen arsenites and trimethylene hydrogen arsenite, preparation of, 807.
Acidolysis, of ethyl stearate with adipic acid, kinetics of, 193; with succinic acid, kinetics of, 193.
— significance of, in the polyesterification reaction, 193.
Acids, alkylphosphonic, esters of, and their parachors, 787.
— β-amino, investigations relating to, 113; new synthesis of alkyl esters of, 637; series, the Curtius reaction in, 847. (See also Amino acids).
— arylsulfonamidophosphoric, preparation, 649.
— 7-benz[a]anthracenemethane-phosphonic, and 12-methyl-7-benz[a]anthracenemethanephosphonic, synthesis of, 131.
— 1-(3-bromopropyl)-2-oxo-cyclopentanecarboxylic, and 1-(3-chloropropyl)-2-oxo-cyclopentanecarboxylic, preparation of ethyl esters, 419.
— citraconic and mesaconic and their esters, condensation with divinyl, 301.
— dialkoxyphosphinylsuccinic, and their esters, preparation of, 821.
— dialkylphosphorous, viscosity and structure of, 485; addition to the amide and esters of methacrylic acid, 657; addition of, to unsaturated dibasic acids and their esters, 821; and their acid chlorides, addition to α-epoxides, 837.
— dicarboxylic, significance of decarboxylation of, in polycondensation process, 509.
— diphenylstibinic, preparation of, 103.
— glycolphosphorous, esters of, 697.
— hydroxyalkylphosphonic, preparation of, 837.
— inorganic, hexadecyl esters of, 483.
— 1-methylcyclohexane-1,2-dicarboxylic, and their esters, cis-trans isomerism of, 301.
— unsaturated carboxylic, synthesis and properties of α-alkoxyethyl esters of, ("acylals"), 453.
— unsaturated dibasic, and their esters, addition of dialkylphosphorous acids to, 821.
Acrylate, methyl, polymerization of, in the absence of light, 265.

Acrylic esters, addition of phenyl- and alkyl-phosphonous esters to, 803.
Acylals, hydrolysis of, 453.
"Acylals" (α-alkoxyethyl esters of unsaturated carboxylic acids), synthesis and properties of, 453.
Adipic acid, (See Acid, adipic).
Adsorbents, porous structure of, 549.
Adsorption, of ethylene and propylene on active charcoal, 877.
– of gaseous mixtures. Part 2. Adsorption of ethylene and propylene on active charcoal, 877.
– of mixtures, on heterogeneous surfaces, dynamics of, 69.
Adsorptional centers in the reaction of hydrogenation of acetylene on metallic nickel, elucidation of role of, 577.
Alcohols, acetylenic, researches on, 955; preparation of, 691.
– aliphatic, indirect vinylation of, 959.
– higher fatty, synthesis of vinyl ethers of, 465.
– kinetics of dehydration of, in presence of tricalcium phosphate, 177.
– reaction of sulfides of phosphorous with, 661.
– role of, in the synthesis of hydrocarbons from carbon monoxide and hydrogen, 601.
– and titanium, tetrachloride, preparation of trichloroalkoxytitanes from, 907.
Aldehydes, addition of O,O-diethyl hydrogen phosphorothioite to, 825
Aliphatic alcohols, indirect vinylation of, 959.
Alkanes, catalytic alkylation of ammonia with halogen derivatives of, 599.
– isomerization of, in presence of $AlCl_3$ under a pressure of hydrogen, 171.
– halogen derivatives of, catalytic alkylation of ammonia with, 473.
α-Alkoxyethyl esters of unsaturated carboxylic acids ("acylals"), synthesis and properties of, 453.
(Alkoxymethyl) ethylene hydrogen arsenites, preparation of mixed esters derived from, 807.
Alkyl esters, of β-amino-acids, new synthesis of, 637.
Alkyl halides, action of, on sodium, potassium, and silver dialkyl phosphorothioates, 755.
– effect of the nature of the halogen and of its position in the molecule on amination of, 599.
– magnesium, mechanism of reaction of β-silicoalkyl halides with, 591.
– β-silico, mechanism of reaction with magnesium alkyl halides, 591.
Alkylisoxazoles, synthesis of, from β-chlorovinyl ketones, 97.
Alkyl-lithium and β-silicohalides, synthesis of silicohydrocarbons from, 985.
Alkyl phenyl acetals, preparation, properties, hydrolysis of, 959.
Alkylation, catalytic, of ammonia with halogen derivatives of alkanes, and cycloalkanes, 473; of alkanes and cyclanes, 599.
Alkylphosphonic acids, esters of, and their parachors, 787.
Alkylphosphonoselenonic esters, mechanism of addition to alkylphosphonous esters, 797.
Alkyl-phosphonous esters, addition to methacrylic and acrylic esters, 803.
Alkylphosphonothionic esters, mechanism of addition to alkylphosphonous esters, 797.
Alloys, heat of formation of, 255.
– thermodynamic study of, 255.
– of aluminum and magnesium, and of bismuth and antimony, intracrystalline liquation, by the microhardness method, 251.
– of the magnesium-cadmium system, mechanical properties of, 383.
– magnesium-silicon, electron density of, 31.
Allylsilanes, synthesis and properties of, 537.
Allyltributylsilane, synthesis and properties of, 537.
Aluminum chloride, isomerization of alkanes in presence of, under a pressure of hydrogen, 171.
– reactions of methylcyclohexane and toluene in contact with, 149.
Aluminum-magnesium alloys, intracrystalline liquation of, by the micro-hardness method, 251.
Aluminum oxide catalysts, of dehydration reactions, effect of dimensions of elementary crystallites on the porosity and activity of, 325.
Amide of methacrylic acid, addition of dialkylphosphorous acid to, 657.
Amides of sulfuric acid and trichlorophosphazosulonaryls, new data on the chemistry of, 649.
Amination of alkyl halides, effect of the nature of the halogen and of its position in the molecule on, 599.
Amines, primary aromatic, action of, on vinyl allyl ketones, 923.
Aminoacetals, synthesis of, 185.
β-Amino acid series, the Curtius reaction in, 847.
– investigations relating to, 113.
– new class of coordination compounds of chromium with, 269.
– new synthesis of alkyl esters of, 637.
β-Aminobutyric acid, synthesis and reactions of, 113.
β-Amino-β-cyclohexylpropionic acid, synthesis of, and some of its derivatives, 293.
β-Aminopropionic acid, β-(β-naphthyl), and certain of its derivatives, synthesis and characterization of, 123.
2-Aminopropionic acid, 2-(2'-naphthyl)-, and its pyrimidine derivatives, 285.
Amino phosphonic esters, new method for the synthesis of, 831.
α-Aminopyridine, action of, on vinyl allyl ketones, 923.

2-Aminopyridines, ultra-violet absorption spectra of, 673.
Ammonia, catalytic alkylation of, with halogen derivatives of alkanes, and cycloalkanes, 473; of alkanes and cyclanes, 599.
Analogs, of phenol compounds of the inert gases, 23.
Anilides, preparation of, 649.
Anthracene derivatives, investigation of, 135.
— 9, 10-dichloro-, relative activities of the meso carbon atom in reactions with oxidizing agents, 135.
Antimony-bismuth alloys, intracrystalline liquation of, by the micro-hardness method, 251.
— compounds, aromatic organo-, synthesis of, by the aid of arylazoformates, 103.
Aqueous solutions, coordination numbers and hydration of the ions, Li^+, Na^+, K^+, Cl^-, Br^-, and I^-, in, 389.
— coordination numbers of ions, Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} in, 585.
Aromatic arsenic-organic compounds, synthesis of, through arylazocarboxylic salts, 911
— nitroso compounds, addition of 2,3-dimethyl-1,3-butadiene, 1-phenyl-1,3-butadiene, and of bi-1-cyclohexen-1-yl to, 539.
— organo-antimony compounds, synthesis of, by the aid of arylazoformates, 103.
Arsenic-organic compounds, aromatic, through arylazocarboxylic salts, 911.
Arsenites, (alkoxymethyl)ethylene-, and trimethylene-, hydrogen, preparation of mixed esters derived from, 807.
Arsenochloridites, preparation, properties of, 807.
Arylazocarboxylic salts, arsenic-organic compounds through, 911.
Arylazoformates, use in synthesis of aromatic organo-antimony compounds, 103.
4-Aryldihydrouracils, preparation of, 637.
1-Aryl-3-hydroxypyrrolidines, synthesis of, 695.
N-Aryl quaternary salts of quinoline derivatives, 347.
N-Arylquinaldine derivatives, asymmetrical carbocyanines from 499.
N-Arylquinaldine, asymmetrical carbocyanines from, 667.
N-Arylquinocyanines, preparation, 491.
N-Arylquinolinium salts, preparation and properties, 347.
Aryl-substituted γ-piperidones, synthesis of, 923.
Arylsulfonamidophosphoric acids, preparation, 649.
Ash tuffs, and their weathering products, electron microscopic investigations of, 395.
Atoms, thermochemistry and structure of, 245.
Azoformates, aryl, use of, in synthesis of aromatic organo-antimony compounds, 103.

Barium ions, coordination numbers of, in aqueous solutions, 585.
Beketov, N. N., session of the Division of Chemical Sciences devoted to the 125th anniversary of the birth of, 543.
Bentonite clays, electron-microscopic investigation of, 395.
β-Benzamidobutyric acid, preparation of, 118.
7-Benz[a]anthracenemethane-phosphonic, and 12-methyl-7-benz[a]anthracenemethane phosphonic acids, synthesis of, 131.
Benzene, nitroso, addition of 1,3-butadiene to, 523.
— addition of cyclohexa-1,3-diene to, 613.
Benzene vapor, sorption by natural sorbents, 553.
Benzothiazole, derivatives, unsymmetrical carbocyanines from, 499.
N-Benzoylated imidazolidone derivatives, preparation of, 847.
Biisocrotyl, catalytic hydrogenation of, 409.
Binary metallic systems, heat of formation of, 255.
— thermodynamic study of, 255.
Binary systems, adsorption on active charcoal, 877.
— metallic, thermodynamic study of, 255.
Bismuth-antimony alloys, intracrystalline liquation, by the micro-hardness method, 251.
Bismuth-cadmium system, thermodynamic study of, 255.
"Biuret" metallo-organic complexes, of protein breakdown products, 963.
"Biuret" organometallic protein complexes, 855.
Bonds, contact, and the new structural theory, 215.
— double, conjugated system of, catalytic hydrogenation of doubly unsaturated compounds with, 409.
Boric esters, viscosity-structure relationships for, 773.
Boron, thermochemistry of, 245.
Buta-1,3-diene, addition of nitrosobenzene to, 339.
— addition to nitrosobenzene, 523.
— addition of, to p-nitrosotoluene, 607.
— reaction with 1-chloro-1-nitrosocyclohexane, 355.
— 2,3-dimethyl, addition to aromatic nitroso compounds, 539.
— 1-phenyl, addition to aromatic nitroso compounds, 539.
Butane, cyclo-, series, synthesis of hydrocarbons, 319.
n-Butene, effect of the carbon monoxide concentration on the hydrocondensation reactions with carbon monoxide, 157.
N-2-Butenylaniline, preparation, 523.
Butindiol, tetramethyl, synthesis of mono- and diacetals of, 955.
A. M. Butlerov's theory of chemical structure, ninety years of, 1.
— teaching, the development of organic chemistry in the light of, 13.
Butylsilane, triallyl, synthesis and properties of, 537.
Butyric acid, β-amino, synthesis and reactions of, 113.

Cadmium-lead system, thermodynamic study of, 255.
— magnesium system, mechanical properties of alloys of, 383.
— tin system, thermodynamic study of, 255.
— zinc system, thermodynamic study of, 255.

Calcium ions, coordination numbers of, in aqueous solutions, 585.
Capillary condensation, calculation of, in the vicinity of points of contact of spherical particles, 885.
– of vapors in highly disperse systems, studies of, 885.
Caprolactam, vinyl, polymerization of, in presence of hydrogen peroxide, 633.
– vinyl, synthesis, hydrolysis, polymerization of, 627.
– vinyl, synthesis and transformations of, 633.
Carbon monoxide, catalytic hydrocondensation of, with olefins, 157; 859; 939.
– concentration, effect of, on the hydrocondensation reactions with propene and n-butene, 157.
– and hydrogen, role of oxygen-containing compounds in the synthesis of hydrocarbons from, 601.
Carbonic ester groupings, presence in oxycellulose, and their effect on the estimation of uronic carboxyl groups, 199.
Carbostyril derivatives, tautomerism of, 747.
Carboxyl groups, uronic, estimation of, and effect of carbonic ester groupings in oxycellulose, 199.
Carcinogenic compounds, derivatives of, preparation, 131.
Catalysis, dehydrogenation, poisoning of catalysts with a low content of active metal, on a carrier under conditions of, 567.
Catalytic alkylation of ammonia with halogen derivatives of alkanes, and cycloalkanes, 473.
– of ammonia with halogen derivatives of alkanes and cyclanes. Part 2. Effect of the nature of the halogen and of its position in the molecule on amination of alkyl halides, 599.
Catalysts, Al_2O_3, of dehydration reactions, effect of dimensions of elementary crystallites on the porosity and activity of, 325.
– for desulfurization of gasoline, 469.
– determination of specific surface of, 327.
– poisoning of, with a low content of active metal on a carrier under conditions of dehydrogenation catalysis, 567.
– vanadium, study of oxygen exchange on, by the use of O^{18}, 403.
Catalytic dehydrogenation, of ethylbenzene, role of inert diluents on, 559.
– of ethylcyclohexane fraction of Maikop gasoline, preparation of styrene by, 477.
Carbocyanines, asymmetrical, from N-arylquinaldine and indolenine, 667.
– asymmetrical, from derivatives of N-arylquinaldine and of benzothiazole, 499.
Carbocyclic ketones, reaction of, with 1-acetyl-1-cyclohexene, 423.
Catalytic hydrocondensation of carbon monoxide with olefins. Communication 7. Effect of the carbon monoxide concentration on the hydrocondensation reactions of carbon monoxide with propene and n-butene, 157.
– of carbon monoxide with olefins. Communication 8. Hydrocondensation of carbon monoxide with 2-methylpropene, 859.
– of carbon monoxide with olefins. Com.9. Reaction of methanol and ethanol with ethylene, 939.
Catalytic hydrogenation of biisocrotyl, 409.
– of doubly unsaturated compounds having a conjugated system of double bonds. Communication 1. Hydrogenation of biisocrotyl, 409.
Catalytic oxidation of ethylene on magnesium chromite, 55.
– of phosphine over a wide range of temperatures, 895.
Cathodic polarization of iron in oxidizing media, 377.
Cell, sorption, behavior, and meniscus of liquid obtained by capillary condensation of vapor in, 885.
Cellobiose, α-octyl-acetyl, optical activity of, 333.
Cellulose, chemical transformations of, due to its oxidation with sodium hypochlorite, 681.
Cellulose macromolecule, chemical changes produced by oxidizing agents, 199.
– chemical transformations of, caused by oxidants, 681.
Cellulose triacetate, optical activity of, 333.
Charcoal, active, adsorption of ethylene and propylene on, 877.
– adsorption of phosphine on, 895.
– porous structure of, 549.
Chemical changes produced in the cellulose macromolecule by oxidizing agents. Communication 6. The presence in oxycelluloses of carbonic ester groupings and their effect on the estimation of uronic carboxyl groups, 199.
Chemical structure, theory of, ninety years of A. M. Butlerov's, 1.
– and pharmacological activity, conference on relation between, 223.
Chemical transformations of cellulose macromolecules caused by oxidants. Com.7. Chemical transformations of cellulose due to its oxidation with sodium hypochlorite, 681.
Chemistry of amides of sulfuric acid and trichlorophosphazosulfonaryls, new data on, 649.
Chemistry and physical chemistry, of high-molecular compounds, conference on, 997.
Chemistry, organic, development of, in the light of A. M. Butlerov's teaching, 13.
Chemistry of pyrazolone derivatives, new data on, 917.
Chemistry, Soviet, toward new successes of, 873.
Chlorides, cyclic acid, and mixed esters derived from (alkoxymethyl)ethylene hydrogen arsenites and trimethylene hydrogen arsenite, preparation of, 807.
– trialkoxytitanium, new method of synthesizing, 81.
– triethoxytitanium, transesterification of, 81.
1-Chloro-1-nitrosocyclohexane, reaction with buta-1,3-diene and cyclohexa-1,3-diene, 355.
Chloroprene, polymerization of, 41.

β-Chlorovinyl ketones, synthesis of isoxazoles from, 97.
Chromatography, on heterogeneous surfaces, theory of, 63.
– theory of, on heterogeneous surfaces, 69.
Chromium, new class of coordination compounds with amino-acids, 269.
Cis-trans isomerism of 1-methylcyclohexane-1,2-dicarboxylic acids and their esters, 301.
Citraconic acid and esters, condensation with divinyl, 301.
Clays, bentonite, electron-microscopic investigation of, 395.
Complex compounds of phosphorous esters. Communication 1. Compounds with copper, silver and gold salts, 729.
– Communication 2. Complex compounds with platinous salts, 737.
– Communication 3. Complex compounds with mercury salts, 743
Compounds containing conjugated links, polymerization of, 41.
– with conjugated double bonds, kinetics of polymerization of, 265.
Condensation, capillary, calculation of, in the vicinity of points of contact of spherical particles, 885.
– of vapors in highly disperse systems, studies of, 885.
Condensation, of cyclic β-diketones with vinyl ketones and transformations of the resulting products, 309.
– of divinyl with citraconic and mesaconic acid and their esters, 301.
– poly, process, significance of decarboxylation of dicarboxylic acids in, 509.
– products of 2-methoxybuta-1,3-diene with methylcyclohex-1-en-6-one and methyl methacrylate, 643.
Conjugated double bonds, kinetics of polymerization of compounds with, 265.
– links, polymerization of compounds containing, 41.
– system of double bonds, catalytic hydrogenation of doubly unsaturated compounds with, 409.
"Contact bonds" and the "new structural theory", 215.
Coordination compounds, new class of, of chromium with amino-acids, 269.
– stability of and the periodic law of D. I. Mendeleev, 239.
Coordination numbers and hydration of the ions Li^+, Na^+, K^+, Cl^-, Br^-, and I^- in aqueous solutions, 389.
– of the ions Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} in aqueous solutions, 585.
Copper "biuret" complexes of protein breakdown products, absorption spectra of, 963.
Copper compounds, in catalytic oxidation of phosphine, 895.
Copper salts, compounds of phosphorous esters with, 729.
Crystal-hydrates of uranyl nitrate and chloride, free energy and heat of dehydration of, 981.
Crystals, experimental study of electron density, 31.
Crystallites, elementary, dimensions of, effect on the porosity and activity of Al_2O_3 catalysts of dehydration reactions, 325.
Current, alternating, effect on the electrodeposition of nickel, 399.
The Curtius reaction in the β-amino acid series, 847.
Cyanine dyes, preparation, 491.
– studies in the field of, 667.
– Communication 1. Symmetrical N-arylquinocyanines, 491.
– Communication 2. Unsymmetrical carbocyanines from derivatives of N-arylquinaldine and of benzothiazole, 499.
Cyanines, N-arylquino-, preparation, 491.
Cyclanes, catalytic alkylation of ammonia with halogen derivatives of, 599.
Cycloalkanes, catalytic alkylation of ammonia with halogen derivatives of, 473.
Cyclic acid chlorides and mixed esters derived from (alkoxymethyl)ethylene hydrogen arsenites and trimethylene hydrogen arsenite, preparation of, 807.
Cyclic compounds, researches on the stereochemistry of, 301.
Cyclic β-diketones, condensation of with vinyl ketones, and transformations of the resulting products, 309.
Cyclic esters, of phosphorochloridous acid, preparation of, 697.
– of phosphorochloridous acid, preparation of, 705.
– mixed, of phosphorous acid, preparation of, 697.
– N-substituted, of phosphoramidous acid, 713.
– of triethylene glycol with succinic, adipic and sebacic acids, preparation of, viscosity, 773.
Cyclic ketones, unsaturated, reaction of phosphorous trichloride with, 517.
Cyclic, poly-, compounds related to the steroids, synthesis of 643.
Cyclobutane, 1-methyl-3-ethyl-, synthesis of, 319.
Cyclobutane series, synthesis of hydrocarbons of, 319.
Cyclohexa-1,3-diene, addition of, to nitrosobenzene, 613.
– reaction with 1-chloro-1-nitroso-cyclo-hexane, 355.
– 1-ethinyl, and its derivatives, 691.
1-Cyclohexene, 1-acetyl, reaction of carbocyclic ketones with, 423.
Cyclohexane, 1-chloro-1-nitroso, reaction with buta-1,3-diene and cyclohexa-1,3-diene, 355.
bi-1-Cyclohexen-1-yl, addition to aromatic nitroso compounds, 539.
β-Cyclohexylpropionic acid, β-amino-, synthesis of, and some of its derivatives, 293.
Cyclohexyl radical, phosphorous acid derivatives containing, 723.
Cyclopentane carboxylic acids, 1-(3-bromo-propyl)-

2-oxo-, and 1-(3-chloropropyl)-2-oxo-, preparation of ethyl esters, 419.
Cyclopentane, methyl, B ring, synthesis of ketones with, 427.

Decarboxylation, of dicarboxylic acids in the polycondensation process, significance of, 509.
Dechlorination of hexachlorethane by trialkyl phosphites, 819.
Decolorizing earths, sorption of benzene vapor by, 553.
Dehyration and thermal properties of perhydrates of sodium carbonate, 589.
– of alcohols in presence of tricalcium phosphate, kinetics of, 177.
– reactions, effect of dimensions of elementary crystallites on the porosity and activity of Al_2O_3 catalysts of, 325.
Dehydrogenation catalysis, poisoning of catalysts with a low content of active metal, on a carrier, under conditions of, 567.
– catalytic, of the ethylcyclohexane fraction of Maikop gasoline, preparation of styrene by, 477.
– catalytic, role of inert diluents on, 559.
Density, π-electron, and interatomic distances, distribution of, 359.
– electron, in crystals, experimental study of, 31.
– electron, of Mg_2Si, 31.
Desorption curves, determination of heats of adsorption of sites on a solid surface from, 63.
Desulfurizing action of Troshkov kaolin, 469.
Dialkenyls, γ-halogeno-, behavior of, in the Grignard-Würtz synthesis, 949.
Dialkoxy derivatives, α,β- and β,β'- of diethyl sulfides, synthesis of, 459.
β,β-Dialkoxydiethylmercaptals, preparation, properties, 459.
Dialkoxyphosphinylformamides, N,N-diethyl-, dipole moments of, 781.
Dialkoxyphosphinylsuccinic acids and their esters, preparation, 821.
Dialkylacetals, synthesis of, 617.
Dialkylphosphinic esters, mechanism of addition to alkylphosphonous esters, 797.
(Dialkylphosphinyl)formamides, N,N-diethyl-, preparation of, 759.
Dialkylphosphorochloridates, preparation of, 819.
Dialkyl phosphorothioates, sodium, potassium, and silver, action of alkyl halides on, 755.
Dialkylphosphorous acids, addition to the amide and esters of methacrylic acid, 657.
Dialkylphosphorous acids, addition of, to unsaturated dibasic acids and their esters, 821.
– viscosity and structure of, 485.
– and their acid chlorides, addition to α-epoxides, 837.
Dialkyldithiophosphates, preparation of, 661.
Diatomite, electron-microscopic investigation of, 395.
Dibasic acids, unsaturated, and their esters, addition of dialkylphosphorous acids to, 821.
Dibenzhydrylthiophen, structure and certain properties of, 993.
Dibutyl vinylphosphonate, preparation of, 813.
Dicarboxylic acids, aromatic, preparation, structure, properties, of polyesters of, 505.
– significance of decarboxylation of, in polycondensation process, 509.
9,10-Dichloroanthracene, relative activities of the meso-carbon atom in reactions with oxidizing agents, 135.
Diene, buta-1,3-, addition of nitrosobenzene to, 339.
– addition of, to p-nitrosotoluene, 607.
– reaction with 1-chloro-1-nitrosocyclohexane, 355.
1,3-Diene, cyclohexa-, addition of, to nitrosobenzene, 613.
– reaction with 1-chloro-1-nitroso-cyclo-hexane, 355.
– 1-ethinylcyclohexa-, and its derivatives, 691.
– 2-methoxy-, structure of the products of condensation of, with methylcyclohex-1-en-6-one and methyl methacrylate, 643.
– 2-methoxybuta-, structure of the products of condensation of, with methylcyclohex-1-en-6-one and methyl methacrylate, 643.
Diene hydrocarbons, reactions of, with nitrosocompounds, 339.
– reactions with nitrosocompounds, 355.
– reactions of, with nitroso compounds, 523.
– reactions of, with nitroso-compounds, 607.
– reactions, of, with nitroso-compounds, 613.
– reactions of, with nitroso-compounds, 539.
Diene synthesis, reactions with vinylphosphonic esters, 813.
N,N-Diethyl(dialkoxyphosphinyl)formamides, dipole moments of, 781.
– preparation of, 759.
O,O-Diethyl-hydrogen phosphorothioite, addition of, to ketones and aldehydes, 825.
Diethyl sulfides, some new α,β- and β,β'-dialkoxy derivatives of, 459.
Differential isotope method, study of the active surface of nickel, by means of, 577.
3,6-Dihydro-2-phenyl-1,2,2H-oxazine, reduction, 523.
– 1,2,2H-oxazine derivatives, preparation, 539.
Diisobutylene, preparation of, 165.
β-Diketones, cyclic, condensation of, with vinyl ketones, and transformations of the resulting products, 309.
Diluents, inert, role of, on catalytic dehydrogenation of ethylbenzene, 559.
Di-(3-methylcyclobutyl) methane, synthesis of, 319.
2,3-Dimethyl-1,3-butadiene, addition to aromatic nitroso compounds, 539.
Dimethylene-neopentylcarbinol, monohalide derivatives of, splitting-off of hydrogen halide from, 165.

β,β-Diphenylpropionylmesitylene, enolization, benzoylation, methoxymethylation, 92.
Diphenylstibinic acids, preparation, 103.
Dipole moments of N,N-diethyl(dialkoxyphosphinyl) formamides, 781.
Disperse systems, studies of capillary condensation of vapors in, 885.
Dithious acid, phosphorochlorido, ethylene ester of, and related substances, 437.
Divinyl, condensation of, with citraconic and mesaconic acid and their esters, 301.
Double bonds, conjugated, kinetics of polymerization of compounds with, 265.
– conjugated system of, catalytic hydrogenation of doubly unsaturated compounds with, 409.
Dyes, cyanine, preparation, 491; studies in the field of, 667.
Dyestuffs chemistry. Cyanine dyes. Communication 1. Symmetrical N-arylquinocyanines, 491.
– Cyanine dyes. Communication 2. Unsymmetrical carbocyanines from derivatives of N-arylquinaldine and benzothiazole, 499.
– Studies in the field of cyanine dyes. Part 3. Asymmetrical carbocyanines from N-arylquinaldine and indolenine, 667.
Dynamics, of the adsorption of mixtures on heterogeneous surfaces, 69.

Earths, decolorizing, sorption of benzene vapor by, 553.
– diatomaceous, industrial bleaching, Fuller's, sorption of benzene vapor by, 553.
Electrochemical behavior of iron in oxidizing media. Communication 3. Cathode polarization of iron in oxidizing media, 377.
Electrodeposition, of nickel, effect of alternating current on, 399.
Electron absorption spectra of polystyrene and its derivatives, 903.
π-Electron density and interatomic distances, distribution of, 359.
Electron density, in crystals, experimental study, 31.
– of Mg_2Si, 31.
Electron-microscopic investigation of ash-tuffs and their weathering products, bentonite clays and diatomites, 395.
– investigations of natural sorbents, 395.
Elements of the third group of D. I. Mendeleev's system, application of the rule of thermochemical logarithmics, 245.
Enolates, sodium, stereoisomeric, 87.
Enolization, of β,β-diphenylpropionylmesitylene, 92.
α-Epoxides, addition of dialkylphosphorous acids and their acid chlorides to, 837.
Ester, ethylene, of phosphorochloridodithious acid and related substances, 437.
Esters, acrylic and methacrylic, addition of phenyl- and alkyl-phosphonous esters to, 803.
Esters, α-alkoxyethyl, of unsaturated carboxylic acids ("acylals"), synthesis and properties of, 453.
– alkyl, of β-amino-acids, new synthesis of, 637.
– of alkylphosphonic acids, and their parachors, 787.
– certain alkylphosphonothionic, alkylphosphonoselenonic, dialkylphosphinic and alkylphosphonous, and the mechanism of addition to alkylphosphonous esters, 797.
– alkylphosphonous, mechanism of addition to certain alkylphosphonothionic, alkylphosphonoselenonic, dialkylphosphinic, esters, 797.
– amino phosphonic, new method for the synthesis of, 831.
– of citraconic and mesaconic acid, condensation with divinyl, 301.
– cyclic, of phosphorochloridous acid, preparation, 697.
– cyclic, of phosphorochloridous acid, preparation, 705.
– cyclic, of triethylene glycol with succinic, adipic, and sebacic acids, preparation of, viscosity, 773.
– of dialkoxyphosphinylsuccinic acids, preparation of, 821.
– ethyl, of 7-benz[a]anthracenemethanephosphonic, and 12-methyl-7-benz[a]anthracenemethanephosphonic acids, synthesis of, 131.
– ethyl, of 1-(3-bromopropyl)-2-oxocyclopentanecarboxylic acid, and of 1-(3-chloropropyl)-2-oxo-cyclopentanecarboxylic acid, preparation of, 419.
Esters of ethylphosphonous acid, and some of their reactions. Communication 1. Full esters of ethylphosphonous acid, 765.
– ethylphosphonous, and some of their reactions, 843.
– of "glycolphosphorous acids". Communication 1. Compounds having five-, seven- and eight-membered rings, 697.
– of "glycolphosphorous acids". Communication 2. Compounds having a six-membered ring, 705.
– hexadecyl, of certain inorganic acids, 483.
– α-hydroxy phosphonothionic, preparation of, 825.
– ketophosphonothionic, preparation of, 825.
– of methacrylic acid, addition of dialkylphosphorous acid to, 657.
– of 1-methylcyclohexane-1,2-dicarboxylic acids, cis-trans isomerism of, 301.
– mixed, derived from (alkoxymethyl)-ethylene hydrogen arsenites and trimethylene hydrogen arsenite, preparation of, 807.
– mixed, of phosphorous acid, preparation of, 723.
– mixed cyclic, of phosphorous acid, preparation of, 697.
– partial, of ethylphosphonous acid, 843.
– phosphinic, new method for the synthesis of, 657; and their thio analogs, new method for the synthesis of, 825; and their thio analogs, new method for the synthesis of, 831.

– phosponic and phosphinic and their thio analogs, new method for the synthesis of, 821.
– phosphonic, and their thio analogs, new method for the synthesis of, 825.
– phosphonic, and their thio analogs, new method for the synthesis of, 831.
– phosphonic and phosphinic, and their thio analogs, synthesis of, 803.
– phosphorous, compounds with copper, silver, and gold, 729.
– phosphorous, complex compounds of, 737.
– phosphorous, complex compounds of, 743
– phosphorous, phosphoric, phosphorothionic, and boric, viscosity-structure relationships, 773.
– poly, of certain aromatic dicarboxylic acids, preparation, structure, properties, 505.
– poly, macromolecules, reactions with each other, 967.
– N-substituted cyclic, of phosphoramidous acid, 713
– thiophosphinic, new method for the synthesis of, 657.
– of unsaturated dibasic acids, addition of dialkylphosphorous acids to, 821
– vinylphosphonic, phosphonoethylation and diene-synthesis reactions with, 813.
Esterification, poly, reaction, significance of acidolysis in, 193.
Ethane, hexachloro-, dechlorination of, by trialkyl phosphites, 819.
Ethanol, reaction with ethylene, 939.
Ethanolamines, vinyl ethers of, synthesis and reactions of, 185.
Ethers, of isatin, preparation of, hydrolysis, 443.
– vinyl, of ethanolamines, synthesis and reactions of, 185.
– vinyl, of higher fatty alcohols, synthesis of, 465.
– vinyl, synthesis of sulfur compounds by the aid of, 459.
1-Ethinylcyclohexa-1,3-diene and its derivatives, 691.
Ethylation, phosphono-, and diene synthesis reactions with vinylphosphonic esters, 813.
Ethylbenzene, catalytic dehydrogenation of, role of inert diluents on, 559.
Ethylcyclohexane fraction of Maikop gasoline, preparation of styrene by catalytic dehydrogenation of, 477.
Ethyl esters, of 7-benz[a]anthracenemethanephosphonic and 12-methyl-7-benz[a]anthracenemethanephosphonic acids, synthesis of, 131.
– of 1-(3-bromopropyl)-2-oxocyclopentanecarboxylic acid, and of 1-(3-chloropropyl)-2-oxo-cyclopentanecarboxylic acid, preparation of, 419.
Ethyl stearate, kinetics of acidolysis with adipic and succinic acids, 193.
Ethylene, adsorption on active charcoal, 877.
– catalytic oxidation of, on magnesium chromite, 55.
– reaction of methanol and ethanol with, 939.
– ester of phosphorochloridodithious acid, and related substances, 437.
– glycol, polyesters with aromatic dicarboxylic acids, preparation, structure, properties of, 505.
– glycol, syntheses of acetals of, 617.
Ethylphosphonous acid, esters of, and some of their reactions, 765.
– esters and some of their reactions. Communication 2. Partial esters of ethylphosphonous acid, 843.
– acid, partial esters of, 843.

Fatty alcohols, higher, synthesis of vinyl ethers of, 465.
Formamides, N,N-diethyl (dialkoxyphosphinyl), preparation of, 759.
Formamides, N,N-diethyl(dialkoxyphosphinyl), dipole moments of, 781.
Formates, arylazo-, use of, in synthesis of aromatic organo-antimony compounds, 103.
Free energy and heat of dehydration of crystal-hydrates of uranyl nitrate and chloride, 981.

Gaseous mixtures, adsorption of, 877.
Gasoline, desulfurization by Troshkov kaolin, 469.
– Maikop, preparation of styrene by catalytic dehydrogenation of the ethylcyclohexane fraction of, 477.
Gel, silica, porous structure of, 549.
Glucose, α-pentyl-acetyl, optical activity of, 333.
Glycols, acetylenic, researches on, 955.
Glycol, ethylene, syntheses of acetals of, 617.
– ethylene, polyesters with aromatic dicarboxylic acids, preparation, structure, properties of, 505.
– triethylene, cyclic esters of, with succinic, adipic, and sebacic acids, preparation and viscosity, 773.
"Glycol-phosphorous acids," esters of, 697; 705.
Gold salts, compounds of phosphorous esters with, 729.
Grignard-Würtz synthesis, behavior of γ-halogeno di-alkenyls in, 949.

Halides, alkyl, action of, on sodium, potassium, and silver dialkyl phosphorothioates, 755.
– effect of the nature of the halogen and of its position in the molecule on amination of, 599.
– magnesium alkyl, mechanism of reaction with β-silicoalkylhalides, 591.
– mercuric, reaction with phosphorous ester, 743.
– β-silicoalkyl, mechanism of reaction with magnesium alkyl halides, 591.
Halogen, effect of the nature of, and of its position in the molecule on amination of alkyl halides, 599.
– derivatives of alkanes, and cycloalkanes, catalytic alkylation of ammonia with, 473.
– derivatives of alkanes and cyclanes, catalytic alkylation of ammonia with, 599.
γ-Halogeno di-alkenyls, behavior of, in the Grignard-Würtz synthesis, 949.
Halo, mono-derivatives of dimethylneopentylcarbinol, [2-Cl(I)-2,4,4-trimethylpentane], splitting-off of the elements of hydrogen halide from, 165.
– mono-derivatives of hydrocarbons of the series C_nH_{2n+2}, splitting off of the elements of hydrogen halide, 165.

Hardness, micro, method of studying intracrystalline liquation, 251.

Heat of dehydration and free energy of crystalhydrates of uranyl nitrate and chloride, 981.

Heat of formation of alloys, 255.

Heat of formation of binary metallic systems, 255.

Heats of adsorption of sites on a solid surface, determination from desorption curves, 63.

Heats of formation, of phenol compounds of inert gases, 28.

Heats of solution, of LiCl, NaCl, KCl, NaBr · $2H_2O$, NaI · $2H_2O$ and $N(CH_3)_4Br$ in aqueous solutions of HCl, measurement of, 390.

Heavy oxygen, use of, in study of oxygen exchange on vanadium catalysts, 403.

Heterocyclic compounds. XXIII. Action of primary aromatic amines and α-aminopyridine on vinyl allyl ketones Synthesis of aryl-substituted γ-piperidones and 1-(α-pyridyl)-4-piperidones, 923.

– XXIV. Transformations of 1-phenyl-2,5-dimethyl-4-piperidone, 933.

Heterogeneous surfaces, dynamics of adsorption of mixtures on, 69.

– theory of chromatography on, 63; 69.

Hexachlorethane, dechlorination of, by trialkyl phosphites, 819.

Hexadecyl esters of certain inorganic acids, 483.

n-Hexane, isomerization of, 171.

High-molecular compounds, conference on the chemistry and physical chemistry of, 997.

– Part 52. Reactions of polyester macromolecules with each other, 967.

Hydration, and coordination numbers of the ions, Li^+, Na^+, K^+, Cl^-, Br^-, and I^- in aqueous solutions, 389.

Hydrocarbons of the cyclobutane series, synthesis of, 319.

Hydrocarbons, diene, reactions of, with nitroso-compounds, 339; 355; 523; 539; 607; 613.

– role of oxygen-containing compounds in the synthesis of, from carbon monoxide and hydrogen, 601.

– of the series C_nH_{2n+2}, mono-halo derivatives of, splitting-off of the elements of hydrogen halide, 165.

– silico-, synthesis of, from β-silicohalides and alkyllithium, 985.

Hydrocondensation of carbon monoxide with 2-methylpropene, 859.

– catalytic, of carbon monoxide with olefins, 157, 859; 939.

Hydrogen arsenites, (alkoxymethyl)ethylene-, and trimethylene-, preparation of mixed esters derived from, 807.

Hydrogen halide, splitting-off of the elements of, from monohalo derivatives of dimethylneopentylcarbinol, [2-Cl(I)-2,4,4-trimethylpentane], 165; splitting-off of the elements of, from monohalo derivatives of hydrocarbons of the series C_nH_{2n+2}, 165.

Hydrogen, isomerization of alkanes under a pressure of, in presence of $AlCl_3$, 171.

Hydrogen peroxide, polymerization of vinylcaprolactam in presence of, 633.

– study of systems containing, 589.

Hydrogenation of acetylene on metallic nickel, elucidation of the role of various adsorptional centers, 577.

– catalytic, of biisocrotyl, 409.

– catalytic, of doubly unsaturated compounds having a conjugated system of double bonds, 409.

Hydrolysis, of acylals, 453.

Hydroxyalkylphosphonic acids, preparation of, 837.

β-Hydroxyethylalkylacetals, preparation of, 617.

α-Hydroxy phosphonothionic esters, preparation, 825.

Imidazolidone, N-benzoylated derivatives, preparation of, 847.

Indolenine, asymmetrical carbocyanines from, 667.

Inert diluents, role of, on catalytic dehydrogenation of ethylbenzene, 559.

Inert gases, phenol compounds of, and their analogs, 23.

Inorganic acids, hexadecyl esters of, 483.

Interatomic distances and π-electron density, distribution of, 359.

Intra-crystalline liquation, micro-hardness method of studying, 251; nature of the phenomenon of, 251; of alloys of aluminum and magnesium and of bismuth and antimony, by the micro-hardness method, 251.

Ions, Li^+, Na^+, K^+, Cl^-, Br^-, and I^-, coordination numbers and hydration in aqueous solutions, 389.

– Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}, coordination numbers of, in aqueous solution, 585.

Iron, cathodic polarization of, in oxidizing media, 377.

– electrochemical behavior of, in oxidizing media, 377.

Isatin ethers, preparation of, hydrolysis, 443.

– tautomerism of, 443.

Isomerism, cis-trans, of 1-methylcyclohexane-1,2-dicarboxylic acids and their esters, 301.

– of alkanes in presence of $AlCl_3$ under a pressure of hydrogen. Communication 1. Isomerization of n-hexane, 171.

– of n-hexane, 171.

Isomorphism, of phenol compounds of inert gases, 27.

Isotope, differential method, study of the active surface of nickel by means of, 577.

Isoxazoles, synthesis of, from β-chlorovinyl ketones, 97.

Kaolin, electron-microscopic investigation of, 395.

Kaolin, Troshkov, desulfurizing action of, 469.

Ketones, addition of O,O-diethyl hydrogen phosphorothioite to, 825.

- carbocyclic, reaction of, with 1-acetyl-1-cyclohexene, 423.
- β-chlorovinyl, synthesis of isoxazoles from, 97.
- tetracylic, having a methylcyclopentane B ring, synthesis of, 427.
- unsaturated cyclic, reaction of phosphorus trichloride with, 517.
- vinyl, condensation of with cyclic β-diketones, and transformations of the resulting products, 309.
- vinyl allyl, action of primary aromatic amines and α-aminopyridine on, 923.

Ketophosphonothionic esters, preparation of, 825.

Kinetics of the dehydration of alcohols in presence of tricalcium phosphate, 177.

- of the polymerization of compounds containing a conjugated link. Polymerization of methyl acrylate, 41.
- of polymerization of compounds with conjugated double bonds. Polymerization of methyl acrylate in absence of light, 265.

Lactam, vinylcapro, synthesis hydrolysis, and polymerization of, 627; synthesis and transformations of 633; polymerization of, in presence of hydrogen peroxide, 633.

Lead-tin system, thermodynamic study of, 255.

Light, absence of, polymerization of methyl acrylate in, 265.

Liquation, intra-crystalline, micro-hardness method of studying, 251; nature of the phenomenon of, 251.

Logarithmics, thermochemical, application of the rule of, to elements of the third group of D. I. Mendeleev's system, 245.

Lomonosov, M. V., 240th anniversary of the birth of, 367.

- session in honor of the bicentenary of the foundation of the science of physical chemistry by, 869.

Macromolecular compounds. Communication 43. Significance of acidolysis in the polyesterification reaction, 193.

- Communication 44. Polyesters of certain aromatic dicarboxylic acids, 505.
- Communication 45. Significance of the decarboxylation of dicarboxylic acids in the polycondensation process, 509.

Macromolecule, cellulose, chemical changes produced by oxidizing agents, 199.

- cellulose, chemical transformations of, caused by oxidants, 681.
- polyester, reactions with each other, 967.

Magnesium alkyl halides, mechanism of reaction of β-silicoalkyl halides with, 591.

Magnesium-aluminum alloys, intracrystalline liquation of, by the micro-hardness method, 251.

Magnesium-cadmium system, mechanical properties of alloys of, 383.

Magnesium chromite, catalytic oxidation of ethylene on, 55.

- sodium silicate, catalytic oxidation of ethylene on, 55.

Magnesium ions, coordination numbers of, in aqueous solutions, 585.

Magnesium-silicon alloy, electron density of, 31.

Mechanism of reaction of magnesium alkyl halides with β-silicoalkyl halides, 591.

Mendeleev, D. I., prizes for 1951, award of, 373.

Mendeleev's system, application of the rule of thermochemical logarithmics to elements of the third group, 245.

Mercaptals, β,β'-dialkoxydiethyl, preparation, properties, 459.

Mercuric halides, reaction with phosphorous esters, 743.

Mercury salts, complex compounds of phosphorous esters with, 743.

Mesaconic acid and esters, condensation with divinyl, 301.

Mesitylene, β,β-diphenylpropionyl, enolization, benzoylation, methoxymethylation, 92.

Meso carbon atom of anthracene and 9,10-dichloroanthracene, relative activities of, in reactions with oxidizing agents, 135.

Mesomerism, or theory of resonance, remarks on, 973.

Metallic systems, binary, heat of formation of, 255.

Metallo-organic "Biuret" complexes of protein breakdown products, 963.

Methacrylic acid, addition of dialkylphosphorous acids to the amide and esters of, 657.

Methacrylic esters, addition of phenyl- and alkylphosphonous esters to, 803.

Methane, di-(3-methylcyclobutyl), synthesis of, 319.

- tetrabutyl, synthesis and properties of, 945.
- tetrapropyl, synthesis and properties of, 945.

Methanol, reaction with ethylene, 939.

2-Methoxybuta-1,3-diene, structure of the products of condensation of, with methylcyclohex-1-en-6-one and methyl methacrylate, 643.

Methyl acrylate, polymerization of, 41; in the absence of light, 265.

Methylallylsilanes, synthesis and properties of, 989.

Methylcyclohexane, reactions in contact with aluminum chloride, 149.

1-Methylcyclohexane-1,2-dicarboxylic acids and their esters, cis-trans isomerism of, 301.

Methyl-cyclohex-1-en-6-one, structure of products of condensation with 2-methoxybuta-1,3-diene, 643.

Methylcyclopentane B ring, synthesis of ketones with, 427.
1-Methyl-3-ethylcyclobutane, synthesis of, 319.
Methylimidazolidone, preparation of, 120.
Methyl methacrylate, structure of products of condensation with 2-methoxybuta-1,3-diene, 643.
2-Methylpropene, hydrocondensation of carbon monoxide with, 859.
1-Methyltrimethylene phosphorochloridite, preparation of, 705.
Micro-hardness method of studying intracrystalline liquation. 1. Nature of the phenomenon of intracrystalline liquation, 251.
Microscope, electron, investigations of natural sorbents, 395.
Mixtures, gaseous, adsorption of, 877.
Molecular weights, of compounds of phosphorous esters with copper, silver, and gold salts, determination of, 729.
Moments, dipole, of N,N-diethyl(dialkoxyphosphinyl) formamides, 781.
Monohalo derivatives of dimethylneopentylcarbinol, [2-Cl(I)]2,4,4-trimethylpentane], splitting-off of the elements of hydrogen halide from, 165.
– of hydrocarbons of the series C_nH_{2n+2} splitting-off of the elements of hydrogen halide, 165.
Montmorillonite clays, electron-microscopic investigation of, 395.

β-Naphthaldehyde, preparation of, 123.
β-(β-Naphthyl)-β-aminopropionic acid and certain of its derivatives, synthesis and characterization of, 123.
2-(2'-Naphthyl)-2-aminopropionic acid and its pyrimidine derivatives, Part 2, 285.
α-Naphthylsilane, triallyl, synthesis and properties of, 537.
Natural sorbents, electron-microscopic investigation of, 395.
Natural sorbents of the Far East. Electron-microscopic investigations of natural sorbents, 395; sorption of benzene vapor by natural sorbents, and the structure of sorbents, 553.
Neopentyl carbinol, dimethyl, monohalide derivatives of, splitting-off of hydrogen halide from, 165.
Nickel, effect of alternating current on electrodeposition of, 399.
– study of active surface of, by means of a differential isotope method, 577.
Nicotine, ultra-violet absorption spectra of some derivatives of, 673.
Nitrosobenzene, addition of buta-1,3-diene to, 339, 523.
Nitrosobenzene, addition of cyclohexa-1,3-diene to, 613.
Nitroso compounds, aromatic, addition of 2,3-dimethyl-1,3-butadiene, 1-phenyl-1,3-butadiene, and of bi-1-cyclohexen-1-yl to, 539.
– reactions, with diene hydrocarbons, 339, 355, 523, 539, 607, 613.
1-Nitrosocyclohexane, 1-chloro, reaction with buta-1,3-diene and cyclohexa-1,3-diene, 355.
p-Nitrosotoluene, addition of buta-1,3-diene to, 607.

α-Octyl-acetyl cellobiose, optical activity of, 333.
Olefins, catalytic hydrocondensation of carbon monoxide with, 157, 859, 939.
– perfluoro, addition reactions of, 279.
Optical activity of cellulose triacetate, α-pentyl-acetyl glucose and α-octyl-acetyl cellobiose, 333.
Organic chemistry, development of, in the light of A. M. Butlerov's teaching, 13.
Organo-antimony compounds, aromatic, synthesis of, by the aid of arylazoformates, 103.
Organometallic "Biuret" protein complexes, 855.
Organo-phosphorous compounds, researches in the field of, 661.
1,2,2H-Oxazine, 3,6-dihydro-2-phenyl, reduction, 523.
Oxazine, ortho-, 3,6-dihydro-derivatives, preparation of, 355.
– 2-phenyl-3,6-dihydro-, preparation from nitrosobenzene and buta-1,3-diene, 339.
– 2-phenyl-3,6-dihydro-, synthesis from cyclohexa-1,3-diene and nitrosobenzene, 616.
Orthoxazine, 2-p-tolyl-3,6-dihydro-, synthesis from buta-1,3-diene and p-nitrotoluene, 607.
1,2,2H-Oxazine, 3,6-dihydro, derivatives, preparation, 539.
Oxazoles, iso, synthesis of, from β-chlorovinyl ketones, 97.
Oxidants, chemical transformations of cellulose macromolecules, caused by, 681.
Oxidation with sodium hypochlorite, chemical transformations of cellulose due to, 681.
Oxidation, catalytic, of ethylene on magnesium chromite, 55
Oxidation, catalytic, of phosphine over a wide range of temperatures, 895.
Oxidizing agents, chemical changes produced in the cellulose macromolecule by, 199.
– relative activities of the meso carbon atom of anthracene and 9,10-dichloroanthracene, in reactions with, 135.
Oxidizing media, cathodic polarization of iron in, 377.
– electrochemical behavior of iron in, 377.
Oxycelluloses, formation from cellulose by sodium hypochlorite oxidation, 681.
– presence of carbonic ester groupings in, and their effect on the estimation of uronic carboxyl groups, 199.
Oxygen-containing compounds, role of, in the synthesis of hydrocarbons from carbon monoxide and hydrogen, 601.
Oxygen exchange, on vanadium catalysts, study of, by the use of O^{18}, 403.
Oxygen, heavy, use of, in study of oxygen exchange on vanadium catalysts, 403.

Parachors, of esters of alkylphosphonic acids, 787.
Partial esters of ethylphosphonous acid, 843.
Particles, spherical, calculation of capillary condensation in the vicinity of points of contact of, 885.
Pentane, 2-Cl(I)-2,4,4-trimethyl, splitting-off of the elements of hydrogen halide from, 165.
α-Pentyl-acetyl glucose, optical activity of, 333.
Perfluoro-olefins, addition reactions of, 279.
Perhydrates of sodium carbonate, thermal properties and dehydration of, 589.
Periodic law of D. I. Mendeleev and the stability of co-ordination compounds, 239.
Pharmaceutical chemistry. Investigations relating to β-amino acids, synthesis and reactions of β-aminobutyric acid, 113.
Pharmacological activity, and chemical structure, conference on relation between, 223.
Phenol compounds, of the inert gases and their analogs, 23.
4-Phenylamino-2-buten-1-ol, preparation 523.
1-Phenyl-1,3-butadiene, addition to aromatic nitroso compounds, 539.
2-Phenyl-3,6-dihydro-ortho-oxazine, preparation from nitrosobenzene and buta-1,3-diene, 339.
1-Phenyl-2,5-dimethyl-4-piperidone, transformations of, 933.
2-Phenyl-3,6-endoethyleno-3,6-dihydro-orthoxazine, synthesis from cyclohexa-1,3-diene and nitrosobenzene, 616.
Phenyl-phosphonous esters, addition to methacrylic and acrylic esters, 803.
1-Phenylpyrrole, reduction of, 531.
1-Phenyl-3-pyrroline, preparation, reduction, 523.
Phosphates, dialkyldithio, preparation of, 661.
Phosphazosulfonaryls, trichloro, new data on the chemistry of, preparation, hydrolysis, acidolysis, aminolysis, arylaminolysis, 649.
Phosphine, catalytic oxidation of, over a wide range of temperatures, 895.
Phosphinic esters, dialkyl, mechanism of addition to alkylphosphonous esters, 797.
– new method for the synthesis of, 657.
– and their thio analogs, synthesis of, 803.
– and their thio analogs, new method for the synthesis of, 821, 825, 831.
Phosphinylformamides, N,N-diethyl-dialkyl, preparation of, 759.
– N,N-diethyl, dialkoxy, dipole moments of, 781.
Phosphinylsuccinic acids, dialkoxy-, and their esters, preparation of, 821.
Phosphites, trialkyl, dechlorination of hexachloroethane by, 819.
Phosphonic acids, esters of, and their parachors, 787.
– hydroxyalkyl, preparation of, 837.
– synthesis of 7-benz[a]anthracenemethane- and 12-methyl-7-benz[a]anthracene-, 131.
Phosphonic esters and their thio analogs, synthesis of, 803.
– and their thio analogs, new method for the synthesis of, 821, 825, 831.
– amino, new method for the synthesis of, 831.
"Phosphonoethylation" and diene-synthesis reactions with vinylphosphonic esters, 813.
Phosphonous acid, ethyl, esters of, and some of their reactions, 765.
Phosphonous alkyl esters, mechanism of addition to alkylphosphonous esters, 797.
Phosphonous esters, phenyl- and alkyl-, addition to methacrylic and acrylic esters, 803.
Phosphonoselenonic, alkyl, esters, mechanism of addition of alkylphosphonous esters, 797.
Phosphonothionic, alkyl, esters, mechanism of addition to alkylphosphonous esters, 797.
Phosphoramidous acid, N-substituted cyclic esters of 713.
Phosphoric esters, viscosity-structure relationships for, 773.
Phosphorochloridates, dialkyl, preparation of, 819.
Phosphorochloridodithious acid, ethylene ester of, and related substances, 437.
Phosphorochloridous acid, cyclic esters of, preparation, 697, 705.
Phosphorothioates, dialkyl, sodium, potassium and silver, action of alkyl halides on, 755.
Phosphorothioite, O,O-diethyl hydrogen, addition of, to ketones and aldehydes, 825.
Phosphorothionic esters, viscosity-structure relationships for, 773.
Phosphorous acids, dialkyl, addition of, to the amide and esters of methacrylic acid, 657.
– dialkyl, and their acid chlorides, addition to α-epoxides, 837.
– viscosity and structure of, 485.
– esters of, 705.
– mixed cyclic esters of, preparation, 697.
– mixed esters of, preparation, 723.
– derivatives containing a cyclohexyl radical, 723.
– glycol-, esters of, 697.
Phosphorous esters, complex compounds of, 729, 737, 743.
– compounds with copper, silver, and gold, 729.
– viscosity-structure relationships for, 773.
Phosphorus-organic compounds, researches in the field of, 661.
Phosphorus, sulfides of, reaction with alcohols, 661.
Phosphorus, trichloride, reaction with unsaturated cyclic ketones, 517.
Photographic science, conference on the basic problems of, 225
Physical chemistry, session in honor of the bicentenary of the foundation of the science of, by M. V. Lomonosov, 869.

γ-Piperidones, aryl-substituted, synthesis of, 923.
4-Piperidone, 1-phenyl-2,5-dimethyl, transformations of, 933.
4-Piperidones, 1-(α-pyridyl), synthesis of, 923.
Platinous chloride, complex compounds of phosphorous esters with, 737.
Platinous salts, complex compounds of phosphorous esters with, 737.
Platinum dehydrogenation catalysts on a carrier, poisoning by organic sulfur compounds, 567.
Polarization, cathodic, of iron in oxidizing media, 377.
Polycondensation process, significance of decarboxylation of dicarboxylic acids in, 509.
Polycyclic compounds related to the steroids, synthesis of, 301, 423, 427, 643.
Polyesters of certain aromatic dicarboxylic acids, preparation, structure, properties, 505.
Polyester macromolecules, reactions with each other, 967.
Polyesterification reaction, significance of acidolysis, 193
Polymers, three-dimensional, properties of, 507.
Polymerization, hydrolysis, and synthesis of vinylcaprolactam, 627.
- kinetics of, of compounds with conjugated double bonds, 265.
- of chloroprene, 41.
- of compounds containing a conjugated link, 41.
- of methyl acrylate, 41.
- of methyl acrylate in the absence of light, 265.
- of vinylcaprolactam in presence of hydrogen peroxide, 633.
Polypeptides, preparation of, 649.
Polystyrene and its derivatives, electron absorption spectra of, 903.
Porous structure of active charcoal, silica gel, 549.
- of adsorbents, 549.
Porosity and activity of Al_2O_3 catalysts of dehydration reactions, effect of dimensions of elementary crystallites, 325.
Potassium iodide, compounds of, with phosphorous esters-platinous salts, complexes, 737.
Propene, effect of the carbon monoxide concentration on the hydrocondensation reactions with carbon monoxide, 157.
- 2-methyl, hydrocondensation of carbon monoxide, with, 859.
Propionic acid, β-amino-β-cyclohexyl-, and some of its derivatives, synthesis of, 293.
- β-(β-naphthyl)-β-amino-, and certain of its derivatives, synthesis and characterization of, 123
Propylene, adsorption on active charcoal, 877.
Principle, trans-effect, conference on, 863.
Prizes, D. I. Mendeleev, award of, for 1951, 373.
Protein breakdown products, metallo-organic "Biuret" complexes, of, 963.
Protein complexes, organometallic "Biuret", 855.
Proto-acids, protein, properties of, 855.
Pyrazolone derivatives, new data on the chemistry of, 917.
Pyridine, ultra-violet absorption spectra of some derivatives of, 673.
- α-amino, action of, on vinyl allyl ketones, 923.
- 2-amino, ultra-violet absorption spectra of, 673.
1-(α-Pyridyl)-4-piperidones, synthesis of, 923.
Pyrimidine derivatives, of 2-(2′-naphthyl)-2-aminopropionic acid, 285.
Pyrrole, 1-phenyl, reduction of, 531.
Pyrrolidines, 1-aryl-3-hydroxy, synthesis of, 695.
3-Pyrroline, 1-phenyl, preparation, 523.

Quaternary salts, N-aryl, of quinoline derivatives, 347.
Quinaldine, N-aryl, asymmetrical carbocyanines from, 667.
- N-aryl, derivatives, unsymmetrical carbocyanines, from 499.
Quinocyanines, N-aryl, preparation, 491.
Quinoline derivatives, N-aryl quaternary salts of, 347.
- studies of, 347.
Quinolinium salts, N-aryl, preparation and properties, 347.

Resonance, theory of, letter to the editor relating to, 547.
- or mesomerism, remarks on, 973.

Salts, arylazocarboxylic, arsenic-organic compounds through, 911.
- N-aryl quaternary, of quinoline derivatives, 347.
- N-aryl quinolinium, preparation and properties, 347.
- of copper, silver, and gold, compounds of phosphorous esters with, 729.
- of mercury, complex compounds of phosphorous esters with, 743.
- platinous, complex compounds of phosphorous esters with, 737.
Silane, allyltributyl, synthesis and properties of, 537.
- dimethyl-di-(methylallyl), synthesis and properties of, 989.
- methyldi-(methylallyl), synthesis and properties of, 989.
- methyltri-(methylallyl), synthesis and properties of, 989.
- tetrahexyl, synthesis and properties of, 945.
- triallylbutyl, synthesis and properties, of, 537.
- triallyl-α-naphthyl, synthesis and properties of, 537.
- trimethylcyclopentadienyl, synthesis and properties of, 989.
- trimethylbut-3-enyl, synthesis and properties of, 989.
Silanes, allyl, synthesis and properties of, 537.
- methylallyl, synthesis and properties of, 989.
Silica gel, porous structure of, 549.
β-Silicoalkyl halides, mechanism of reaction with magnesium alkyl halides, 591.

β-Silicohalides and alkyl-lithium, synthesis of silicohydrocarbons from, 985.
Silicohydrocarbons, synthesis of, from β-silicohalides and alkyl-lithium, 985.
– unsaturated, synthesis and properties of, 989.
Silicon-magnesium alloy, electron density of, 31.
Silver salts, compounds of phosphorous esters with, 729.
Sodium carbonate, perhydrates of, thermal properties and dehydration of, 589.
Sodium enolates, stereoisomeric, 87.
– hypochlorite, chemical transformations of cellulose due to oxidation with, 681.
– silicate-magnesium chromite catalyst, catalytic oxidation of ethylene on, 55.
Solid surfaces, heats of adsorption, determination from desorption curves, 63.
Solubility, in the reciprocal system $CaSO_4-KCl-H_2O$ at 55°, 45.
– in ternary systems, 45.
Solution, heats of, of LiCl, NaCl, KCl, $NaBr \cdot 2H_2O$, $NaI \cdot 2H_2O$ and $N(CH_3)_4Br$ in aqueous solutions of HCl, measurement of, 390.
Solutions, aqueous, coordination numbers and hydration of the ions, Li^+, Na^+, K^+, Cl^-, Br^-, and I^- in, 389.
– aqueous, coordination numbers of ions Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} in, 585.
Sorbents, natural, electron-microscopic investigation of, 395.
– of the Far East, 395.
– sorption of benzene vapor by, 553.
– structure of, 553.
Sorption of benzene vapor by natural sorbents, and the structure of sorbents, 553.
– cell, meniscus of liquid obtained by capillary condensation of vapor in, 888.
Soviet chemistry, toward new successes of, 873.
Specific surface, of catalysts, determination of, 327.
– of elementary crystallites, effect of, on the porosity and activity of Al_2O_3 catalysts of dehydration reactions, 325.
Spectra, electron absorption of polystyrene and its derivatives, 903.
Sphericle particles, calculation of capillary condensation in the vicinity of points of contact of, 885.
Stability, of coordination compounds, periodic law of D. I. Mendeleev and, 239.
Stereochemistry, of cyclic compounds, researches on, 301.
Stereoisomeric sodium enolates, 87.
Steroid compounds and related substances, synthesis of, 309.
Steroids, synthesis of polycyclic compounds related to, 301, 423, 427, 643, 309.
Stibinic acids, diphenyl, preparation of, 103.
Strontium ions, coordination numbers of, in aqueous solutions, 585.
Structural theory, new, answer to the critics of, 205.
– contact bonds and, 215.
Structure, chemical and pharmacological activity, conference on relation between, 223.
– chemical, theory of, ninety years of A. M. Butlerov's 1.
– and viscosityof dialkyl phosphorous acids, 485.
– and certain properties of dibenzhydrylthiophen, 993.
– and thermochemistry of atoms, 245.
– porous, of active charcoal, silica gel, 549.
– porous, of adsorbents, 549.
– of the products of condensation of 2-methoxybuta-1,3-diene with methylcyclohex-1-en-6-one and methyl methacrylate, 643.
– of sorbents, 553.
– viscosity relationship for phosphorous, phosphoric, phosphorothionic and boric esters, 773.
Styrene, from catalytic dehydrogenation of ethylbenzene, role of inert diluents, 559.
– poly, and its derivatives, electron absorption spectra of, 903.
– preparation of, by catalytic dehydrogenation of the ethylcyclohexane fraction of Maikop gasoline, 477.
Styril, carbo-, derivatives, tautomerism of, 747.
N-Substituted cyclic esters of phosphoramidous acid, 713.
Succinic acid, kinetics of acidolysis of ethyl stearate with, 193
Succinic acids, dialkoxyphosphinyl-, and their esters, preparation of, 821.
Sulfides, diethyl, some new α,β- and β,β'-dialkoxy derivatives of, 459.
– of phosphorus, reaction of, with alcohols, 661.
Sulfonaryls, trichlorophosphazo, new data on the chemistry of, preparation, acidolysis, aminolysis, arylaminolysis, hydrolysis, 649.
Sulfur compounds, synthesis of, by the aid of vinyl ethers, 459.
– organic, poisoning of platinum catalysts on carrier by, 567.
Sulfur, removal from gasoline by Troshkov kaolin, 469.
Surfuric acid, new data on the chemistry of amides of, and trichlorophosphazosulfonaryls, 649.
Surface, active, of nickel, study of by means of a differential isotope method, 577.
Surfaces, heterogeneous, dynamics of adsorption of mixtures on, 69.
– heterogeneous, theory of chromatography, 69.
– solid, heats of adsorption, determination from desorption curves, 63.
Symmetrical N-arylquinocyanines, preparation, 491.
Syntheses of acetals of ethylene glycol, 617.
Synthesis and characterization of β-(β-naphthyl)-β-aminopropionic acid and certain of its

derivatives. Communication 1, 123.
– and polymerization of vinylcaprolactam, 627.
– and properties of α-alkoxyethyl esters of unsaturated carboxylic acids ("acylals"), 453.
– and properties of allylsilanes: triallyl-α-naphthylsilane, triallylbutylsilane, and allyltributylsilane, 537.
– and properties of tetrapropylmethane, tetrabutylmethane, and tetrahexylsilane, 945.
– and properties of unsaturated silicohydrocarbons: dimethyl-di-(methylallyl) silane, methyldi-(methylallyl)silane, methyltri-(methylallyl)silane, tetra-(methylallyl)silane, trimethylcyclopentadienylsilane, and trimethylbut-3-enylsilane, 989.
– and reactions, of β-aminobutyric acid, 113.
– and reactions of vinyl ethers of ethanolamines. Communication 2. The synthesis of aminoacetals, 185.
– and transformations of vinylcaprolactam. Part 1. Polymerization in presence of hydrogen peroxide, 633.
– new, of alkyl esters of β-amino-acids, 637.
– of β-amino-β-cyclohexylpropionic acid and of some of its derivatives, 293.
– of aminophosphonic esters, new method for, 831.
– of aromatic arsenic-organic compounds through arylazocarboxylic salts, 911.
– of aromatic organo-antimony compounds by the aid of arylazoformates, 103.
– of aryl-substituted γ-piperidones and 1-(α-pyridyl)-4-piperidones, 923.
– of 7-benz[a]anthracenemethanephosphonic and 12-methyl-7-benz[a]anthracenemethane phosphonic acids, 131.
– Grignard-Würtz, behavior of γ-halogeno di-alkenyls in, 949.
– of hydrocarbons, from carbon monoxide and hydrogen, role of oxygen-containing compounds in, 601.
Synthesis of hydrocarbons of the cyclobutane series. Part 2. 1-Methyl-3-ethylcyclobutane and di-(3-methylcyclobutyl) methane, 319.
– of isoxazoles from β-chlorovinyl ketones, 97.
– of 1-methyl-3-ethylcyclobutane and di-(3-methylcyclobutyl) methane, 319.
– of mono- and di-acetals of tetramethylbutindiol, 955.
– of phosphinic and thiophosphinic acid esters, new method for, 657.
– of phosphonic and phosphinic esters and their thio analogs, new methods for, 825.
– of phosphonic and phosphinic esters and their thio analogs, new methods for, 831.
– of polycyclic compounds related to the steroids, 301, 309, 423, 427, 643.
– of silicohydrocarbons from β-silicohalides and alkyllithium, 985.
– of sulfur compounds by the aid of vinyl ethers. Communication 5. Some new α,β- and β,β'-dialoxyderivatives of diethyl sulfides, 459.
– of tetracyclic ketones having a methyl-cyclopentane B ring, 427.
– of trialkoxytitanium chlorides, new method of, 81.
– of the vinyl ethers of higher fatty alcohols, 465.
Systems, binary, adsorption on active charcoal, 877.
– binary, metallic, thermodynamic study of, 255.
– cadmium-zinc, cadmium-lead, cadmium-tin, bismuth-cadmium, tin-zinc and lead-tin, 255.
– $CaSO_4$–KCl–H_2O at 55°, solubility in, 45.
– containing hydrogen peroxide, study of, 589.
– disperse, studies of capillary condensation of vapors in, 885.
– ethylene-propylene, adsorption on active charcoals, 877.
– magnesium-cadmium mechanical properties of alloys of, 383.
– ternary, solubility in, 45.
Tautomerism, of isatin, 443.
– of carbostyril derivatives, 747.
Ternary systems, solubility in, 45.
Tetrabutylmethane, synthesis and properties of, 945.
Tetracyclic ketones, having a methyl-cyclopentane B ring, synthesis of, 427.
Tetrafluoroethylene, addition reactions of, 279.
Tetramethylbutindiol, synthesis of mono- and di-acetals of, 955.
Tetrapropylmethane, synthesis and properties of, 945.
Tetrahexylsilane, synthesis and properties of, 945.
Thermal properties and dehydration of perhydrates of sodium carbonate, 589.
Thermochemical logarithmics, application of the rule of, to elements of the third group of D. I. Mendeleev's system, 245.
Thermochemistry and structure of atoms. Part 6. Thermochemistry of boron: application of the rule of thermochemical logarithmics to elements of the third group of D. I. Mendeleev's system, 245.
– of boron, 245.
Thermodynamic study of the systems cadmium-zinc, cadmium-lead, cadmium-tin, bismuth-cadmium, tin-zinc and lead-tin, 255.
Thio analogs, of phosphonic and phosphinic esters, synthesis of, 803, 821, 825, 831.
Thiophen, dibenzhydryl, structure and certain properties of, 993.
Thiophosphinic acid esters, new method for the synthesis of, 657.
Thiophosphates, dialkyldi-, preparation of, 661.
Thiourea, compounds of, with phosphorous esters-platinous salts complexes, 737.
Tin-zinc system, thermodynamic study of, 255.
Titanium chlorides, trialkoxy, new method of synthesizing, 81.

Titanium chlorides, triethoxy, transesterification of, 81.
– tetrachloride, and alcohols, preparation of trichloroalkkoxytitanes from, 907.
Titanes, trichloroalkoxy, preparation of, from titanium tetrachloride and alcohols, 907.
Toluene, p-nitroso-, addition of buta-1,3-diene to, 607.
– reactions in contact with aluminum chloride, 149.
2-p-Tolyl-3,6-dihydro-orthoxazine, synthesis from buta-1,3-diene and p-nitrosotoluene, 607.
Trans-effect principle, conference on, 863.
Transesterification, of triethoxytitanium chlorides, 81.
Triacetate, cellulose, optical activity of, 333.
Trialkoxytitanium chlorides, new method of synthesizing, 81.
Triallylbutylsilane, synthesis and properties of, 537.
Triallyl-α-naphthylsilane, synthesis and properties of, 537.
Transformations and synthesis of vinylcaprolactam, 633.
– of 1-phenyl-2,5-dimethyl-4-piperidone, 933.
Trialkyl phosphites, dechlorination of hexachloroethane by, 819.
Tributylsilane, allyl, synthesis and properidesof, 537.
Tricalcium phosphate, kineticx of dehydration of alcohols in presence of, 177.
Trichloroalkoxytitanes, preparation of, from titanium tetrachloride and alcohols, 907.
Trichlorophosphazosulfonaryls, new data on the chemistry of, hydrolysis, acidolysis, aminolysis, arylaminolysis, preparation of, 649.
Triethoxytitanium chlorides, transesterification of, 81.
Triethylene glycol, cyclic esters of, with succinic, adipic, sebacic acids, preparation of, viscosity, 773.
Trimethylene hydrogen arsenite, preparation of mixed esters derived from, 807.
– phosphorochloridite, preparation of, 705.
Troshkov kaolin, desulfurizing action of, 469.

Ultra-violet absorption spectra of some derivatives of pyridine and nicotine. Part 3, 673.
Uracils, 4-aryldihydro, preparation of, 637.
Uranyl chloride, free energy and heat of dehydration of crystal-hydrates of, 981.
– nitrate, free energy and heat of dehydration of crystal-hydrates of, 981.
Uronic carboxyl groups, estimation of, and effect of carbonic ester groupings, in oxycellulose, 199.

Vanadium catalysts, study of oxygen exchange on by use of O^{13}, 403.
Vapor, benzene, sorption by natural sorbents, 553.
Vapors, studies of capillary condensation of, in highly disperse systems, 885.
Vinyl allyl ketones, action of primary aromatic amines and α-aminopyridine on, 923.
Vinylation, indirect, of aliphatic alcohols, 959.
Vinylcaprolactam, polymerization of in presence of hydrogen peroxide, 633.
– synthesis and polymerization of, 627.
– synthesis and transformations of, 633.
Vinyl ethers, synthesis of sulfur compounds by the aid of, 459.
– of ethanolamines, synthesis and reactions of, 185.
– of higher fatty alcohols, synthesis of, 465.
Vinyl ketones, condensation of, with cyclic β-diketones, and transformations of the resulting products, 309.
Vinylphosphonate, dibutyl, preparation of, 813.
Vinylphosphonic esters, phosphonoethylation and diene-synthesis reactions with, 813.
Viscosity and structure of dialkylphosphorous acids, 485.
Viscosity-structure relationship for phosphorous, phosphoric, phosphorothionic, and boric esters, 773.

INDEX OF EMPIRICAL FORMULAS OF ORGANIC COMPOUNDS

Group C_1

1. II

CH_4O. Methanol, reaction with ethylene, 939.

Group C_2

2. I

C_2H_4. Ethylene, adsorption on active charcoal, 877; reaction with methanol and ethanol, 939.

2. II

C_2H_6O. Ethanol, reaction with ethylene, 939.

2. IV

$C_2H_4O_2PCl$. Product of reaction of ethylene glycol, dimethylaniline, PCl_3, 699.

$C_2H_4S_2PCl$. Chlorido ester obtained by action of phosphorous trichloride on ethanedithiol, 438.

$C_2H_5OTiCl_3$. Trichloroethoxytitane, preparation, 908.

$C_2H_5O_2Cl_2As$. (Chloromethyl)ethylene arsenochloridite, preparation, properties, 809.

$C_2H_5PSCl_2$. 1) Ethylphosphonothionic dichloride, preparation, properties, 769.
2) Product obtained by addition of sulphur to ethylphosphonous dichloride, 800.

$C_2H_7O_2PS$. Product of reaction of P_4S_6 and methanol, 663; product of reaction of P_4S_7 and methanol, 663; product of reaction of P_4S_7 with ethanol, 663.

2. V

$C_2H_5OPS_2Ba$. Barium salt of dithiane, preparation, 439.

Group C_3

3. I

C_3H_6. 1) Propene, hydrocondensation of carbon monoxide with, 157.
2) Propylene, adsorption on active charcoal, 877.

3. II

C_3H_8O. n-Propanol, role in the synthesis of hydrocarbons from carbon monoxide and hydrogen, 601.

3. III

$C_3H_5O_3Ag$. Silver lactate, preparation, 952.

$C_3H_7O_3P$. Ethylene methyl phosphite, preparation, properties, action of alkyl halides, 699.

$C_3H_9O_2P$. Methyl hydrogen ethylphosphonite, preparation, properties, 843.

3. IV

$C_3H_6O_2AsCl$. Trimethylene arsenochloridite, preparation, properties, 809.

$C_3H_6O_2PCl$. Trimethylene phosphorochloridite, preparation, properties, action of alkyl iodides, 707.

$C_3H_7OTiCl_3$. Trichloro-n-propoxytitane, preparation, 908.

$C_3H_7O_2TiCl_3$. Trichloro-β-methoxyethoxytitane, preparation, 909.

$C_3H_9O_2PS_2$. Product of reaction of P_4S_6 and methanol, 663; product of reaction of P_4S_7 with methanol, 663.

3. V

$C_3H_9O_3PAuCl$. Complex compound of trimethyl phosphite and AuCl, preparation, 734.

$C_3H_9O_3PCl_2Pt$. Product of reaction of methanol with $PtCl_2 \cdot PCl_3$, 739.

$C_3H_9O_3PHgBr_2$. Product of reaction of mercuric bromide with trimethyl phosphite, 744.

$C_3H_9O_3PHg_2Cl_4$. Product of reaction of mercuric chloride with trimethyl phosphite, 743.

Group C_4

4. I

C_4H_8. n-Butene, hydrocondensation of carbon monoxide with, 157.

4. II

$C_4H_6O_2$ Crotonic acid, preparation, 118.

$C_4H_{10}O$. n-Butanol, role in the synthesis of hydrocarbons from carbon monoxide and hydrogen, 601.

4. III

C_4H_5ON. Methylisoxazole, preparation, properties, sodium ethoxide treatment, 99.

C_4H_7ON. 3,6-Dihydro-ortho-oxazine, preparation, properties, 356.

$C_4H_7O_2Ag$. Silver butyrate, preparation, 603.

$C_4H_8OBr_2$. 1,4-Dibromobutanol, preparation, properties, 695.

$C_4H_8ON_2$. Methylimidazolidone, preparation, 121

$C_4H_8S_2Cl_2$. Ethyl 2,2-dichloroethyl sulfide, preparation, properties, 281.

$C_4H_9O_2N$. β-Aminobutyric acid, preparation, 117.

$C_4H_9O_3P$. 1) Ethyl ethylene phosphite, preparation, properties, action of alkyl halides, 700.
2) Ester of glycolphosphorous acid, preparation, 711.
3) Product of reaction of trimethylene phosphorochloridite and methanol, (methyltrimethylene phosphorochloridite), preparation, properties, 707.

$C_4H_9PCl_2$. Isobutylphosphonous dichloride, preparation, properties, 801.

$C_4H_{11}O_2P$. 1) Dimethyl ethylphosphonite, preparation properties, action of cuprous iodide, carbon tetrachloride, 767.
2) Ethyl hydrogen ethylphosphonite, preparation, properties, 844.

$C_4H_{11}O_4P$. 1) Dimethyl 2-hydroxyethylphosphonate, preparation, properties, 840.
2) Product of reaction of ethyl ethylene phosphite and water, 702.

$C_4H_{12}NBr$. Tetramethylammonium bromide, heat of solution, 395.

4. IV

C_4H_4ONBr. 3-Bromomethylisoxazole, preparation, properties, 101.

C_4H_4ONCl. 3-Chloromethylisoxazole, preparation, properties, sodium ethoxide treatment, 101.

C_4H_4ONI. 3-Iodomethylisoxazole, preparation, properties, 101.

C_4H_8ONCl. 3,6-Dihydro-ortho-oxazine hydrochloride, preparation, action of potash, 356.

$C_4H_8O_2PCl$. 1) Product of reaction of 1,4-butanediol, dimethylaniline and PCl_3, 702.
2) 1-Methyltrimethylene phosphorochloridite, preparation, properties, action of alkyl iodides, 707.

$C_4H_8O_2PCl_3$. Methyl ethyltrichloromethylphosphinate, preparation, properties, 771.

$C_4H_8O_3AsCl$. (Methoxymethyl)ethylene arsenochloridite, preparation, properties, hydrolysis, 807; preparation, 811.

$C_4H_8O_3PAg$. Silver salt of a glycolphosphorous acid, preparation, 712.

$C_4H_8O_3PCl$. 2-Chloroethyl ethylene phosphite, preparation, properties, 700; product of reaction of diethylene glycol, PCl_3 and dimethylaniline, 703.

$C_4H_9OS_2P$. Product of reaction of ethyl iodide and o-ethyl ethylene phosphorodithioite, preparation, hydrolysis, 439.

$C_4H_9OTiCl_3$. Trichloroisobutoxytitane, preparation, 908.

$C_4H_{10}OPCl$. Diethylphosphinic chloride, preparation, properties, 801.

$C_4H_{10}O_2PN$. N-substituted cyclic ester of phosphoramidous acid, preparation, properties, 715.

$C_4H_{11}O_2PS$. Product of reaction of 1:1 atomic sulfur-phosphorus melt with ethanol, 665; product of reaction of P_4S_5 with ethanol, 664; product of reaction of P_4S_6 with ethanol, 664.

$C_4H_{11}O_2PS_2$. Product of reaction of P_4S_7 with ethanol, 663.

4. V

$C_4H_{10}O_2PSCl$. Diethylthiophosphoryl chloride, properties, 664.

$C_4H_{10}O_2PHg_2Cl_4$. Product of reaction of mercuric chloride with triethyl phosphite, 745.

4. VI

$C_4H_{10}O_2PNCuI$. Cuprous iodide compound of N-substituted cyclic ester of phosphoramidous acid, 715.

Group C_5

5. II

$C_5H_6O_4$. Monoethyl malonate, preparation, 637.

C_5H_8O. Vinyl allyl ether, properties, 962.

C_5H_9Br. Methylallyl bromide, preparation, properties, 951.

5. III

$C_5H_4ON_2$. 3-Isoxazoleacetonitrile, preparation, properties, 102.

$C_5H_4O_5Ag_2$. Silver salt of α-ketoglutaric acid, preparation, 692.

C_5H_7ON. Ethylisoxazole, preparation, properties, sodium ethoxide treatment, 100.

$C_5H_9O_2Ag$. Silver dimethylacrylate, preparation, 952.

$C_5H_{11}O_3P$. 1) Ester of glycolphosphorous acid, preparation, 709.
2) Phosphite ester, preparation, properties, 708.
3) Product of reaction of methylphosphorodichloridite and 1,4-butanediol, 702.

$C_5H_{11}O_4As$. (Methoxymethyl)ethylene methyl arsenite, preparation, properties, 809.

$C_5H_{13}O_2P$. 1) Isopropyl hydrogen ethylphosphonite, preparation, properties, 844.
2) Propyl hydrogen ethylphosphonite, preparation, properties, 844.

5, IV

$C_5H_{11}OTiCl_3$. Trichloroisoamyloxytitane, preparation, 909.

$C_5H_{10}O_2PCl_3$. Ethyl ethyltrichloromethylphosphinate, preparation, properties, 771.

$C_5H_{10}O_3AsCl$. (Ethoxymethyl)ethylene arsenochloridite, preparation, properties, 808.

$C_5H_{12}O_3PI$. Product of reaction of methyl iodide and ethyl ethylene phosphite, 701.

5. V

$C_5H_{11}O_3PCuI$. Product of reaction of cuprous iodide on reaction product obtained from methylphosphorochloridite and 1,4-butanediol, 702.

5. VII

$C_5H_{18}O_3PPtCl_2S_3N_6$. Product of reaction of thiourea with $PtCl_2 \cdot 2P(OCH_3)_3$, 741.

Group C_6

6. I

C_6H_6. Benzene, formation from toluene, 149.

C_6H_8. Cyclohexa-1,3-diene, preparation, properties, condensation with nitrosobenzene, 614.

C_6H_{12}. Cyclohexane, preparation from methylcyclohexane, 149.

C_6H_{14}. n-Hexane, isomerization, 171.

6. II

$C_6H_{11}Br$. 4-Bromo-4-methylpent-1-ene, preparation, properties, oxidation, 952.

$C_6H_{12}O$. 1) Vinyl sec.-butyl ether, properties, 962.
2) Vinyl tert.-butyl ether, properties, 962.

$C_6H_{12}Br_2$. Isohexene dibromide, preparation, 951.

$C_6H_{14}O_3$. β-Hydroxyethyl ethyl acetal, preparation, properties, hydrolysis, acetalization, 619.

$C_6H_{14}Si$. Allyltrimethylsilane, preparation, properties, 595.

C_6. III

C_6H_5OAs. Product of reaction of potassium phenylazocarboxylate with arsenic trichloride, 913.

C_6H_5ON. Nitrosobenzene, preparation, condensation of cyclohexa-1,3-diene with, 615.

C_6H_9ON. 1) 3,6-Endoethyleno-3,6-dihydroorthooxazine, preparation, benzoylation, 357.
2) Propylisoxazole, preparation, properties, sodium ethoxide treatment, 100.

$C_6H_{11}ON$. 1) Caprolactam, vinylation, 634.
2) 4,5-Dimethyl-3,6-dihydro-orthooxazine, preparation, 357.

$C_6H_{11}O_2Ag$. Silver salt of α-methyl-valeric acid, preparation, properties, 953.

$C_6H_{11}O_4P$. Ester of glycolphosphorous acid, preparation, properties, 711.

$C_6H_{11}O_7P$. Dimethoxyphosphinylsuccinic acid, preparation, properties, 822.

$C_6H_{12}P_2S_6$. Reaction product of phosphorous trichloride and ethane diol, 439.

$C_6H_{13}O_3P$. 1) Butyl ethylene phosphite, preparation, properties, action of bromotriphenylmethane, 700.
2) Propyl trimethylene phosphite, preparation, properties, 708.
3) Phosphite ester, preparation, properties, 708.
4) Ester of glycolphosphorous acid, preparation, 709.

$C_6H_{13}O_4As$. Ethyl (methoxymethyl)ethylene arsenite, preparation, properties, 810.

$C_6H_{15}O_2P$. 1) Diethyl ethylphosphonite, preparation, properties, action of sulfur, cuprous iodide, ethyl iodide, butyl bromide, carbon tetrachloride, ethyl chloroacetate, diethylcarbamoyl chloride, 767; preparation, properties, 800.
2) Ethyl diethylphosphinate, preparation, properties, 770, 800.
3) Butyl hydrogen ethylphosphonite, preparation, properties, 845.
4) Isobutyl hydrogen ethylphosphonite, preparation, properties, 845.

$C_6H_{15}O_2S$. Product of reaction of P_4S_7 with propanol, 665.

$C_6H_{15}O_4P$. Diethyl 2-hydroxyethylphosphonate, preparation, properties, 839.

$C_6H_{15}PS_2$. Product of reaction of P_4S_8 with isopropanol, 666.

$C_6H_{15}ClSi$. β-Chloropropyltrimethylsilane, preparation, properties, 595.

6. IV

$C_6H_2OAsBr_3$. 2,4,6-Tribromophenylarsine oxide, preparation, 915.

C_6H_4OAsBr. Product of reaction of potassium p-bromophenylazocarboxylate with arsenic trichloride, 914.

$C_6H_5N_2SbCl_4$. May's salt, preparation, 109.

$C_6H_6O_3BrSb$. p-Bromophenylstibonic acid, preparation, 110.

$C_6H_6O_4NAs$. Product of reaction of potassium p-nitrophenylazocarboxylate with arsenic trichloride, 914.

$C_6H_6O_5NSb$. p-Nitrophenylstibonic acid, preparation, 109.

$C_6H_{12}ONCl$. 4,5-Dimethyl-3,6-dihyro-ortho-oxazine hydrochloride, preparation, action of potash, 357.

$C_6H_{12}ONI$. 2-Methyl-3,6-dihydro-ortho-oxazine methiodide, preparation, 356.

$C_6H_{12}O_2PCl_3$. Propyl ethyltrichloromethylphosphinate, preparation, properties, 771.

$C_6H_{12}O_3AsCl$. (Isopropoxymethyl)ethylene arsenochloridite, preparation, properties, 809.

$C_6H_{13}OTiCl_3$. Trichloro-n-hexoxytitane, preparation, 909.

$C_6H_{14}O_2PN$. N-Substituted cyclic ester of phosphoramidous acid, preparation, properties, 716, action of methyl iodide, benzyl bromide, water, 718.

$C_6H_{14}O_3ClP$. 2-Chloroethyl ethyl ethylphosphonate, preparation, properties, 841.

$C_6H_{14}O_3PBr$. Product of reaction of ethyl bromide on ethyl ethylene phosphite, 701.

$C_6H_{14}O_3ClP$. Dipropyl phosphorochloridate, preparation, properties, 820.

$C_6H_{14}O_3PN$. Product of reaction of hydrogen peroxide on N-substituted cyclic ester of phosphoramidous acid, 717.

$C_6H_{15}O_2PS$. 1) Diethyl ethylphosphothionate, preparation, properties, 769.
2) Diethyl ethylphosphonothionate, preparation, properties, 800.
3) Product of reaction of P_4S_7 with isopropanol, 665.
4) Product of reaction of P_4S_6 with n-propanol, 665.

$C_6H_{15}O_2PS_2$. 1) Product of reaction of P_4S_5 with ethanol, 664.
2) Product of reaction of P_4S_6 with ethanol, 664.
3) Product of reaction of P_4S_7 with ethanol, 663.
4) Product of reaction of P_4S_7 with isopropanol, 665.
5) Product of reaction of 1:1 atomic sulfur-phosphorus melt with ethanol, 665.
6) Product of reaction of P_4S_7 with propanol, 665.

$C_6H_{15}O_2PSe$. Diethyl ethylphosphonoselenonate preparation, properties, 800.

$C_6H_{15}O_3PS$. 1) Diethyl 2-mercaptoethylphosphonate, preparation, properties, 816.
2) Diethyl-1-hydroxyethylphosphonothionate, preparation, properties, 829.

$C_6H_{18}O_6PtI_2$. Product of reaction of potassium iodide with $PtCl_2 \cdot 2P(OCH_3)_3$, 741.

$C_6H_{10}ONCl$. 3,6-Endoethyleno-3,6-dihydro-ortho-oxazine hydrochloride, preparation, action of potash, 357.

6. V

$C_6H_{15}O_3PCl_2Pt$. Product of reaction of ethanol with $PtCl_2 \cdot PCl_3$, 740.

$C_6H_{13}OSHgCl$. β-Isobutoxyethylmercaptomercuric chloride, preparation, 461.

$C_6H_{18}O_6P_2Cl_2Pt$. Product of reaction of methanol with $PtCl_2 \cdot 2PCl_3$, 740.

$C_6H_{14}O_2PNS$. Sulfur compound of N-substituted cyclic ester of phosphoramidous acid, preparation, properties, 716.

$C_6H_{15}O_3PHgBr_2$. Product of reaction of mercuric bromide with triethyl phosphite, 745.

$C_6H_{15}O_3PHgCl_2$. Product of reaction of mercuric chloride with triethyl phosphite, 744.

$C_6H_{15}O_3P_2Cl_2Pt$. Product of reaction of ethanol with $PtCl_2 \cdot 2PCl_3$, 740.

6. VI

$C_6H_{14}O_2PNCuBr$. Cuprous bromide compound of N-substituted cyclic ester of phosphoramidous acid, preparation, 716.

Group C_7

7. I

C_7H_8. Toluene, reactions in contact with aluminum chloride, 149.

C_7H_{14}. 1) Dimethylcyclopentanes, preparation, properties, 151.

C_7H_{14}. 2) Methylcyclohexane, reactions of, in contact with aluminum chloride, 149.
3) 1-Methyl-3-ethylcyclobutane, cis and trans-preparation, 321.

C_7H_{16}. 2,2-Dimethylpentane, preparation, properties, 951.

7. II

$C_7H_{10}O_3$. 5-Carbomethoxypent-1-en-3-one, preparation, 313.

$C_7H_{12}O$. Hexahydrobenzaldehyde, preparation, 295.

$C_7H_{12}O$. 3-Acetyl-1-methylcyclobutane, preparation, 320.

$C_7H_{13}N$. Aldehyde-ammonia compound of hexahydrobenzaldehyde, preparation, properties, 295.

$C_7H_{16}Si$. Trimethyl-but-3-enylsilane, preparation, properties, 991.

7. III

C_7H_7OAs. Product of reaction of potassium p-tolylazocarboxylate with arsenic trichloride, 914.

C_7H_7OSb. p-Stibosotoluene, preparation, 109.

C_7H_9ON. Amide of 2,3-dihydrobenzoic acid (cyclohexa-1,3-diene-1-carboxylic acid), preparation, 692.

$C_7H_9O_2P$. Methyl hydrogen phenylphosphonite, preparation, 804.

$C_7H_{11}ON$. Isobutylisoxazole, preparation, properties, 100.

$C_7H_{15}O_2Cl$. β-Chloroethyl isopropyl acetal, synthesis and properties, 187.

$C_7H_{15}O_4As$. (Methoxymethyl)ethylene propyl arsenite, preparation, properties, 810.

$C_7H_{17}O_2N$. β-Aminoethyl isopropyl acetal, synthesis and properties, 189.

7. IV

$C_7H_7OSbCl_2$. Oxychloride of p-tolylstibonic acid, preparation, properties, 109.

$C_7H_{16}O_2PN$. N-substituted cyclic ester of phosphoramidous acid, preparation, properties, 717.

$C_7H_{14}O_3AsCl$. (Butoxymethyl)ethylene arsenochloridite, preparation, properties, 809.

$C_7H_{15}O_3PS$. Diethyl-1-hydroxy-2-propenylphosphonothionate, preparation, properties, preparation of phenylhydrazone, semicarbazone, 829.

$C_7H_{17}O_3PS$. Diethyl-1-hydroxy-1-methylethylphosphonothionate, preparation, properties, 829.

7. V

$C_7H_{15}OSHgCl$. β-Isoamyloxyethylmercaptomercuric chloride, properties, 462.

7. VI

$C_7H_{16}O_2PNCuCl$. Cuprous chloride compound of N-substituted cyclic ester of phosphoramidous acid, preparation, 717.

7. VIII

$C_7H_{27}O_3PPtCl_2S_3N_6$. Product of reaction of thiourea with $PtCl_2 \cdot 2P(OC_2H_5)_3$, 741.

Group C_8

8. I

C_8H_8. Stytene, preparation, 477; from catalytic dehydrogenation of ethylbenzene, 559.

C_8H_{10}. 1) Ethylbenzene, catalytic dehydrogenation, 559.
2) Xylenes, preparation, 149.

C_8H_{14}. 1) Biisocrotyl, synthesis, properties, catalytic hydrogenation, 411.
2) 2,5-Dimethyl-2,4-hexadiene, synthesis, catalytic hydrogenation, isomerization, 411.

C_8H_{16}. 1) Dimethylcyclohexane, preparation, 149.
2) Ethylcyclohexane, catalytic dehydrogenation, 477.
3) 4-Methylhept-1-ene, preparation, properties, 951.

8. II

$C_8H_{12}O_3$. Alcohol formed by condensing tetrinic acid with but-1-en-3-one, 317.

$C_8H_{12}O_3$. 1-Methylcyclohexan-4-one-1-carboxylic acid; preparation, 646.

$C_8H_{18}O_3$. β-Hydroxyethylbutylacetal, preparation, properties, hydrolysis, acetalization, 621.

$C_8H_{14}O$. Cyclohexylvinyl ether, synthesis, properties, 455, 465.

$C_8H_{14}O_2$. Diallyl acetal, preparation, properties, 960.

$C_8H_{16}O$. Hexylvinyl ether, preparation, properties, 465.

$C_8H_{14}O_2$. Oxoctenol, preparation, 168.

$C_8H_{14}Si$. Trimethylcyclopentadienylsilane, preparation, properties, 990.

8. III

$C_8H_{11}O_2P$. Ethyl hydrogen phenylphosphonite, preparation, addition to methyl methacrylate, methyl acrylate, ethyl methacrylate, propyl methacrylate, 805.

$C_8H_{13}NO$. Vinylcaprolactam, Preparation, properties, hydrolysis, polymerization, reaction with hydrogen peroxide, 629; N-Vinylcaprolactam, preparation, properties, polymerization, 633.

$C_8H_{15}ON_3$. Semicarbazone of 3-acetyl-1-methylcyclobutane, preparation, 320.

$C_8H_{15}O_7P$. 1) Dimethyl dimethoxyphosphinylsuccinate, preparation, properties, 823.
2) Diethoxyphosphinylsuccinic acid, preparation, properties, 823.

$C_8H_{17}O_2Cl$. β-Chloroethyl isobutyl acetal, synthesis and properties, 188.

$C_8H_{17}O_3P$. 1) Butyl tetramethylene phosphite, preparation, properties, 703.
2) Butyl 1-methyltrimethylene phosphite, preparation, properties, 709.

$C_8H_{17}O_4As$. Butyl(methoxymethyl)ethylene arsenite, preparation, properties, 810.

$C_8H_{17}O_4P$. Ethyl(ethoxycarbonylmethyl) ethylphosphinate, preparation, properties, 771.

$C_8H_{19}O_2N$. β-Aminoethyl isobutyl acetal, preparation and properties, 190.

$C_8H_{19}O_2P$. 1) Propyl ethylpropylphosphinate, preparation, properies, 770.
2) Ethyl butylethylphosphinate, preparation, properties, 770.
3) Dipropyl ethylphosphonite, preparation, properties, action of cuprous iodide, propyl iodide, carbon tetrachloride, ethyl chloroacetate, diethylcarbamoyl chloride, 767.
4) Diisopropyl ethylphosphinite, preparation, properties, action of sulfur, 768.
5) Hexyl hydrogen ethylphosphonite, preparation, properties, 845

$C_8H_{19}O_3P$. (Ethyl)-hexylphosphorous acid, preparation, properties, 488.

8. IV

$C_8H_9O_4NS$. p-Carbomethoxyaminobenzenesulfinic acid, preparation, formation of silver salt, methyl ester, potassium salt, 919.

$C_8H_{11}O_4N_3S$. Hydrazide of p-carbomethoxyaminobenzenesulfonic acid, preparation, formation of compounds with benzaldehyde, acetone, 920.

$C_8H_{18}O_2PN$. N-substituted cyclic ester of phosphoramidous acid, preparation, properties, action of ethyl bromide, 719.

$C_8H_{16}O_2PN$. N-substituted cyclic ester of phosphoramidous acid, preparation, 717.

$C_8H_{18}O_3ClP$. 1) 2-Chloro-1-methylpropyldiethyl phosphite, preparation, properties, 841.
2) Dibutyl phosphorochloridate, preparation, properties, 819.

$C_8H_{18}O_4NP$. β-Diethylphosphoneisobutyramide, preparation, properties, 658.

$C_8H_{19}O_2PS$. 1) Diisopropyl ethylphosphonothionate, preparation, properties, 769.
2) Product of reaction of P_4S_7 with n-butanol, 666.

$C_8H_{19}O_3PS$. 1) Diethyl 1-hydroxybutylphosphonothionate, preparation, properties, 830.
2) Diethyl 2-ethylmercaptoethylphosphonate, preparation, properties, 816.

8. V

$C_8H_{20}O_4P_2S_4Pb$. Lead diethyl dithiophosphate, preparation, ethylation, 664.

8. VI

$C_8H_{16}O_2PNCuBr$. Cuprous bromide compound of N-substituted cyclic ester of phosphoramidous acid, preparation, properties, 717.

Group C_9

9. II

$C_9H_{10}O_3$. Anhydride of trans-1-methylcyclohex-4-ene-1,2-dicarboxylic acid, preparation, isomerization, 305.

$C_9H_{12}O_3$. Cis-1-methylcyclohexane-1,2-dicarboxylic anhydride, preparation, hydrolysis, 304.

$C_9H_{12}O_3$. 1) Methyl-3-methylenopentan-4-one-1-carboxylate, preparation, oxidation, 313.
2) Trans-1-methylcyclohexane-1,2-dicarboxylic acid anhydride, preparation, 305.

$C_9H_{12}O_4$. 1) Diketone formed by condensation of tetrinic acid with but-1-en-3-one, 317.
2) Trans-1-methylcyclohex-4-ene-1,2-dicarboxylic acid, preparation, isomerization, hydrogenation, 304.

$C_9H_{12}O_5$. 1-Methylcyclohexan-4-one-1,3-dicarboxylic acid, preparation, 646.

$C_9H_{10}O$. Benzyl vinyl ether, synthesis, properties, 456.

$C_9H_{14}O_2$. Cyclohexylacrylic acid, preparation, properties, 296.

$C_9H_{14}O_3$. 1-Carbomethoxy-1-methylcyclohexan-4-one, preparation, 646.

$C_9H_{14}O_4$. Trans-1-methylcyclohexane-1,2-dicarboxylic acid, preparation, isomerization, 305.

$C_9H_{14}O_5$. Heptan-3-one-1,6-dicarboxylic acid, preparation, 317.

$C_9H_{18}O$. Heptylvinyl ether, preparation, properties, 465.

$C_9H_{18}Si$. Dimethyl-di-methylallyl silane, preparation, properties, 990.

$C_9H_{20}O_2$. Di-sec-butyl, acetal, preparation, properties, 960.

9. III

C_9H_9ON. Cinnamamide, preparation, 638.

$C_9H_{13}O_2P$. Isopropyl hydrogen phenylphosphonite, preparation, 805.

$C_9H_{16}ON_2$. 5-Cyclohexylglyoxalidone, preparation, 298.

$C_9H_{17}O_2N$. β-Amino-β-cyclohexyl-propionic acid, preparation, properties, 296.

$C_9H_{17}PO_4$. Methyl ester of 1-methyl-3-oxocyclohexylphosponic acid, preparation, 521.

$C_9H_{18}O_4N_2$. Diurethan of propylenediamine, preparation, 121.

$C_9H_{18}O_6As_2$. Trimethylene ester of arsenious acid, preparation, properties, 809.

$C_9H_{19}O_4P$. Propyl(ethoxycarbonylmethyl)-ethylphosphinate, preparation, properties, 771.

$C_9H_{21}SiBr$. Trimethyl-4-bromo-2-methylpentylsilane; (δ-bromide), preparation, properties, 596.

$C_9H_{21}O_2P$. Dibutyl ethylphosphonite, preparation, properties, 768.

$C_9H_{21}O_3P$. 1) Dibutyl methylphosphonate, preparation, properties, 791.
2) Ethyl hexyl methylphosphonate, preparation, properties, 792.

$C_9H_{21}O_5P$. Addition product of diethylphosphorous acid to 1,2-epoxy-3-ethoxypropane, 840.

9. IV

$C_9H_{11}O_4NS$. Methyl p-carbomethoxyaminobenzenesulfonate, preparation, 919.

$C_9H_{11}O_5NS$. Methyl p-carbomethoxyaminobenzenesulfonate, preparation, formation of product with phenylmethylpyrazolone, 919.

$C_9H_{18}O_2PN$. N-substituted cyclic ester of phosphoramidous acid, preparation, properties, action of water, 719.

$C_9H_{19}O_3PS$. Diethyl 1-methyl-3-oxobutylphosphonothionate, preparation, properties, preparation of phenylhydrazone, semicarbazone, 827.

$C_9H_{20}O_3PN$. Diethylamide of ethoxy(ethyl)phosphinylformic acid, preparation, properties, 771.

$C_9H_{20}O_4PN$. 1) N,N-Diethyl(dialkoxyphosphinyl)formamide derivative, dipole moments, 781.
2) N,N-Diethyl(diethoxyphosphinyl)formamide, preparation, properties, 759.

$C_9H_{21}O_2PS_2$. 1) Product of reaction of P_4S_7 with ethanol, 665.
2) Product of reaction of P_4S_7 with isopropanol, 665.
3) Product of reaction of P_4S_9 with n-propanol, 665.

9. V

$C_9H_{21}O_3PAgBr$. Compound of silver bromide and triisopropyl phosphite, preparation, 732.

$C_9H_{21}O_3PAgCl$. Compound of silver chloride and triisopropyl phosphite, preparation, 732.

$C_9H_{21}O_3PAgI$. Compound of silver iodide with triisopropyl phosphite, preparation, 733.

$C_9H_{21}O_3PHgBr_2$. Product of reaction of mercuric bromide with triisopropyl phosphite, 745.

$C_9H_{21}O_3PHgCl_2$. Product of reaction of mercuric chloride with triisopropyl phosphite, 745.

$C_9H_{21}O_3PHgI_2$. Product of reaction of mercuric iodide with triisopropyl phosphite, 745.

$C_9H_{21}O_3P_2Cl_2Pt$. Product of reaction of triisopropyl phosphite with platinous chloride, 740.

9. VIII

$C_9H_{27}O_3PPtS_3N_6Cl_2$. Product of reaction of thiourea with $PtCl_2 \cdot 2P(OC_3H_7\text{-}i)_3$, 742.

Group C_{10}

10. II

$C_{10}H_9N$. 1-Phenylpyrrole, preparation, reduction, 533.

$C_{10}H_{11}N$. 1) 1-Phenyl-3-pyrroline, preparation, reduction, oxidation, 524.
2) Reduction product of 1-phenylpyrrole, 533;
3) Reduction product of 1-phenylpyrrole, 535.

$C_{10}H_{13}N$. 1) 1-Phenylpyrrolidine, preparation, properties, 525; 535.
2) N-2-Butenylaniline, preparation, properties, 526.
3) Reduction product of 1-phenylpyrrole, 533.

$C_{10}H_{14}O_4$. Keto-ester obtained by condensing tetrinic acid with but-1-en-3-one, 317.

$C_{10}H_{15}N$. N-Butylaniline, preparation, properties, benzoylation, 527.

$C_{10}H_{16}O_3$. 1-Carbomethoxy-4-methoxy-1-methylcyclohex-3-ene, preparation, 646.

$C_{10}H_{16}O_6$. Cyclic ester of triethylene glycol with succinic acid, preparation, 779.

$C_{10}H_{20}O$. 1) Isooctylvinyl ether, preparation, properties, 465.
2) Octylvinyl ether, preparation, properties, 465.

$C_{10}H_{20}Si$. Methylallylsilane, preparation, properties, 990.

$C_{10}H_{21}Cl$. 2,2-Dipropylbutyl chloride, preparation, 946.

$C_{10}H_{22}O_2$ Di-tert.-butyl acetal, preparation properties, 960.

10. III

$C_{10}H_7SbO$. β-Stibosonaphthalene, preparation, 110.

$C_{10}H_9O_2As$. β-Naphthyl arsenious acid, preparation, 915.

$C_{10}H_9O_3N$. Methoxymethyl ether of isatin, preparation, 447.

$C_{10}H_9O_5N_3$. 2-(2',4'-Dinitrophenyl)-3,6-dihydro-ortho-oxazine, preparation, 357.

$C_{10}H_{10}O_8N_4$. Picrate of 3,6-dihydro-ortho-oxazine, preparation, 356.

$C_{10}H_{11}ON$. 2-Phenyl-3,6-dihydro-ortho-oxazine, preparation, reduction, 341.

$C_{10}H_{11}O_3N$. N-acetyl-N-phenylglycine, preparation, 342.

$C_{10}H_{13}ON$. 1) 3-Hydroxy-1-phenylpyrrolidine, preparation, acetylation, 696.
2) 2-Phenyl-tetrahydro-ortho-oxazine, preparation, properties, reduction, 342.

$C_{10}H_{13}O_3P$. Product of reaction of methyltrimethylene phosphite and benzyl chloride, 710.

$C_{10}H_{13}O_3N_3$. 1-Carbomethoxy-1-methylcyclohex-2-en-4-one, preparation, 647.

$C_{10}H_{13}O_4As$. (Methoxymethyl)ethylene phenyl arsenite, preparation, properties, 811.

$C_{10}H_{15}ON$. 1) 4-Anilinobutan-1-ol, preparation, properties, 343; 4-anilinobutan-1-ol, properties, 344.
2) Hydrolysis product of N-2-butenylacetanilide, 528.
3) Product of hydrolysis of benzoyl derivative of N-2-butenylaniline, 534.

$C_{10}H_{16}O_2N_2$. 6-Cyclohexyldihydrouracil, preparation, 299.

$C_{10}H_{17}O_5N_3$. Semicarbazone of heptan-3-one-1,6-dicarboxylic acid, preparation, 317.

$C_{10}H_{18}O_3N_2$. β-Ureido-β-cyclohexylpropionic acid, preparation, 299.

$C_{10}H_{19}O_4As$. Cyclohexyl(methoxymethyl)-ethylene arsenite, preparation, properties, 811.

$C_{10}H_{19}O_7P$. Dimethyl diethoxyphosphinylsuccinate, preparation, properties, 823.

$C_{10}H_{21}O_3P$. Dibutyl phosphonate, preparation, properties, 815.

$C_{10}H_{21}O_4P$. 2-Hydroxycyclohexylphosphonate, preparation, properties, 841.

$C_{10}H_{21}O_5P$. Ethyl β-diethylphosphoneisobutyrate, preparation, properties, 659.

$C_{10}H_{23}O_3P$. 1) (Ethyl)-octylphosphorous acid, preparation, properties, 488.
2) Octyl hydrogen ethylphosphonite, preparation, properties, 845.

$C_{10}H_{27}O_4As$. Hexyl (methoxymethyl)ethylene arsenite, preparation, properties, 810.

10. IV

$C_{10}H_{11}O_3N_3S$. Product of hydrolysis of p-acetamidophenyl-N-methyl-pyrazolonesulfone, 921.

$C_{10}H_{14}O_3PN$. N-substituted cyclic ester of phosphoramidous acid, preparation, properties, action of cuprous iodide, 719.

$C_{10}H_{15}O_2PS$. Product of reaction of P_4S_6 with isopropanol, 666.

$C_{10}H_{20}O_3ClP$. 2-Chlorocyclohexyl diethyl phosphite, preparation, properties, 842.

$C_{10}H_{22}O_4NP$. β-Dipropylphosphoneisobutyramide, preparation, 658.

$C_{10}H_{21}O_3Cl_2P$. bis(2-Chloro-1-methylpropyl)-ethyl phosphite, preparation, properties, 841.

$C_{10}H_{21}O_3PS$. Diethyl 1,1-dimethyl-3-oxobutylphosphonothionate, preparation, properties, preparation of phenyl-hydrazone, semicarbazone, 828.

$C_{10}H_{22}O_3PN$. Diethylamide of ethyl(propoxy)phosphinyl formic acid, preparation, properties, 772.

10. V.

$C_{10}H_{22}N_3O_3PS$. Semicarbazone of diethyl 1-methyl-3-oxobutylphosphonothionate, preparation, 827.

10. VI

$C_{10}H_{21}O_3PCuNS$. Complex compound of triisopropyl phosphite with cuprous thiocyanate, preparation, 733.

Group C_{11}

11. I

$C_{11}H_{20}$. Di-(3-methylcyclobutyl)-methane, preparation, properties, 322.

11. II

$C_{11}H_8O$. β-naphthaldehyde, preparation, properties, 125.

$C_{11}H_{13}N$. 1-p-Tolyl-2,5-dihydropyrrole, preparation, oxidation, 609.

$C_{11}H_{14}O_2$. 1) Allyl phenyl acetal, preparation, properties, hydrolysis, 960.
2) Chromanone formed from triketone obtained by condensing 2-methyldihydroresorcinol with but-1-en-3-one, 315.

$C_{11}H_{15}N$. N-Crotyl-p-toluidine, preparation, properties benzoylation, acetylation, 610.

$C_{11}H_{16}Si$. Phenylallyldimethylsilane, preparation, properties, 595.

$C_{11}H_{16}O_3$. 1) Keto-acid formed by condensing 2-methyldihydroresorcinol with but-1-en-3-one, 314.
2) Triketone formed by condensing 2-methyldihydroresorcinol with but-1-en-3-one. 314.

$C_{11}H_{16}O_4$. 1) Dimethyl cis-1-methylcyclohex-4-ene-1,2-dicarboxylate, preparation, isomerization, 306.
2) Dimethyl-trans-1-methylcyclohex-4-ene-1,2-dicarboxylate, preparation, 306.

$C_{11}H_{18}O_4$. Dimethyl trans-1-methylcyclohexane-1,2-dicarboxylate, preparation. 306.

$C_{11}H_{22}O$. Nonylvinyl ether, preparation, properties 465.

$C_{11}H_{26}Si$. Ethyltripropylsilane, preparation, properties, 596.

11. III

$C_{11}H_9O_6N_3$. 2-(3',5'-Dinitrobenzoyl)-3,6-dihydro-orthooxazine. preparation, 357.

$C_{11}H_{10}O_4N_2$. 4-Piperonyldihydrouracil, preparation, 641.

$C_{11}H_{11}NO_2$. Carbostyril methoxymethyl ether, preparation, hydrolysis, isomerization, 748.

$C_{11}H_{11}O_3N$. Ethoxymethyl ether of isatin, preparation, 448.

$C_{11}H_{12}N_2O$. 4-Methyl-6-oxo-2-phenyl-tetrahydropyrimidine. preparation, 119.

$C_{11}H_{13}ON$. 2-p-Tolyl-3,6-dihydro-orthoxazine, preparation, reduction, 608.

$C_{11}H_{13}O_3N$. 1) N-Acetyl-N-tolylglycine, preparation, 609.
2) β-Benzamidobutyric acid, preparation 118.

$C_{11}H_{14}O_2N_2$. β-Benzamidobutyramide, preparation, 119.

$C_{11}H_{14}O_4N_2$. Ethyl ester of β-(3-nitrophenyl)-β-alanine. preparation, 640.

$C_{11}H_{15}ON$. 1) 3-Hydroxy-1-p-tolylpyrrolidine, preparation, 696.
2) 4-p-Tolylaminobut-2-en-1-ol, preparation, benzoylation, acetylation, 608.

$C_{11}H_{15}O_2N$. Ethyl-β-phenyl-β-alanine, preparation, 638.

$C_{11}H_{15}O_3P$. Ester of glycolphosphorous acid, preparation, 711.

$C_{11}H_{17}O_3Br$. Ethyl 1-(3-bromopropyl)-2-oxocyclopentane carboxylate, preparation, properties, 421.

$C_{11}H_{17}O_3Cl$. Ethyl 1-(3-chloropropyl)-2-oxocyclopentanecarboxylate, preparation, properties, 421.

$C_{11}H_{18}O_3N$. N-carbomethoxycyclohexylglyoxalidone, preparation, 299.

$C_{11}H_{18}O_4N_3$. Semicarbazone of diketone formed by condensation of tetrinic acid with but-1-en-3-one, 317.

$C_{11}H_{19}O_3N$. β-Acetamido-β-cyclohexylpropionic acid, preparation, properties, 297.

$C_{11}H_{19}O_4N$. β-Carbomethoxyamino-β-cyclohexylpropionic acid, preparation, properties. 297.

$C_{11}H_{20}O_2N_2$. β-Acetamido-β-cyclohexyl-propionamide, preparation, Hoffmann reaction, 298.

$C_{11}H_{20}O_3N_2$. Amide of β-carbomethoxyamino-β-cyclohexylpropionic acid, preparation, properties, 297.

$C_{11}H_{21}O_3P$. Diethyl 2-methyl-3-cyclohexenylphosphonate, preparation, properties, 816.

$C_{11}H_{21}O_4P$. 1) Ethyl ester of 2,5-dimethyl-3-oxocyclopentylphosphonic acid, preparation, properties, 520.
2) Ethyl ester of 1-methyl-3-oxocyclohexylphosphonic acid, preparation, properties, 521.

$C_{11}H_{21}O_5P$. Allyl-β-diethylphosphoneisobutyrate, preparation, properties, 660.

$C_{11}H_{23}O_5P$. 1) Isopropyl β-diethylphosphoneisobutyrate, preparation, properties, 659.
2) Propyl β-diethylphosphoneisobutyrate, preparation, properties, 659.

$C_{11}H_{25}O_2P$. Nonyl hydrogen ethylphosphonite, preparation, properties, 846.

$C_{11}H_{25}O_3P$. Ethyl octyl methylphosphonate, preparation, properties, 792.

$C_{11}H_{26}SiO$. 6-Trimethylsilyl-3,5-dimethylhexanol, preparation, properties, 597.

11. IV

$C_{11}H_{15}O_4N_3S$. p-Carbomethoxyaminophenylsulfonylhydrazone of acetone, preparation, 921.

$C_{11}H_{16}O_2PN$. N-substituted cyclic ester of phosphoramidous acid, preparation, properties, 720.

$C_{11}H_{17}O_4PS$. Diethyl 3-furyl-1-hydroxy-2-propenylphosphonothionate, preparation, properties, 829.

$C_{11}H_{24}O_4PN$. 1) N,N-Diethyl(dialkoxyphosphinyl formamide derivative, dipole moments. 781.
2) N,N-Diethyl(diisopropoxyphosphinyl)formamide, preparation, properties, 761.
3) N,N-Diethyl(dipropoxyphosphinyl) formamide. preparation. properties, 761.

11. V

$C_{11}H_{21}N_3O_3PS$. Semicarbazone of diethyl 1,1-dimethyl-3-oxobutylphosphonothionate, preparation. 828.

Group C_{12}

12. II

$C_{12}H_{14}N$. N-(β-naphthal)-methylamine, preparation. properties, 126.

$C_{12}H_{14}O_3$. 1-Phenoxyethyl methacrylate, synthesis. properties, 457.

$C_{12}H_{14}O_4$. β-Piperonylacrylate, preparation, 639.

$C_{12}H_{15}N$. 3-Anilinocyclohex-1-ene, preparation, properties, benzoylation, 616.

$C_{12}H_{18}O$. 6-Keto-1,9-dimethyl-Δ'-octalin, preparation, action of magnesium methyl iodide, 645.

$C_{12}H_{18}O_2$. 1) sec.-Butyl phenyl acetal, preparation, properties, 960.
2) tert.-Butyl phenyl acetal, preparation, hydrolysis, properties, 960.

$C_{12}H_{20}Si$. Tetraallylsilane, preparation, properties, 538.

$C_{12}H_{20}O_2$. 6-Keto-1-hydroxy-1,9-dimethyldecalin, preparation, dehydration, 644.

$C_{12}H_{20}O_3$. 1-Cyclohexyloxyethyl methacrylate synthesis, properties, 456.

$C_{12}H_{20}O_6$. Cyclic ester of triethylene glycol with adipic acid. preparation, 778.

$C_{12}H_{22}Si$. Triallylpropylsilane, preparation, properties, 595.

$C_{12}H_{24}O$. Decylvinyl ether, preparation, properties, 465.

$C_{12}H_{26}Si$. Allyltripropylsilane, preparation. properties, 595.

$C_{12}H_{28}Si$. Silicohydrocarbon, properties, 986.

$C_{12}H_{30}Si_2$. 1,4-Di-(trimethylsilyl)-2,3-dimethylbutane, preparation, properties, 596.

12. III

$C_{12}H_{15}O_4N$. Ethyl ester of β-piperonyl-β-alanine, preparation, 639.

$C_{12}H_{10}SbCl_3$. Chlorodiphenylstibine dichloride, preparation, properties, 108.

$C_{12}H_{12}O_8N_4$. Picrate of 3,6-endoethyleno-3,6-dihydro-ortho-oxazine, preparation, 358.

$C_{12}H_{13}ON$. 1) Carbostyril ethoxymethyl ether, preparation, hydrolysis, isomerization, 749.
2) 2-Phenyl-3,6-endoethyleno-3,6-dihydro-orthoxazine, preparation, 615.

$C_{12}H_{13}O_3N$. Propoxymethyl ether of isatin, preparation, properties, 448.

$C_{12}H_{14}O_8N_4$. Picrate of 4,5-dimethyl-3,6-dihydro-ortho-oxazine. 357.

$C_{12}H_{15}ON$. 1) 4-Anilinocyclohex-2-en-1-ol. preparation, acetylation, reduction, 615.
2) N-2-Butenylacetanilide, preparation, properties, oxidation, hydrolysis, 527.
3) 3,6-Dihydro-4,5-dimethyl-2-phenyl-1,2,2H-oxazine, preparation, 540.

$C_{12}H_{15}O_2N$. 3-Acetoxy-1-phenylpyrrolidine, preparation, properties, 696.

$C_{12}H_{15}O_3P$. Cyclohexyl o-phenylene phosphite, preparation, properties, 727.

$C_{12}H_{16}N_2O$. 1-α-Pyridyl-2,5-dimethyl-4-piperidone, preparation, 930.

$C_{12}H_{17}ON$. 2,3-Dimethyl-4-phenylamino-2-buten-1-ol, preparation, properties, acetylation, 540.

$C_{12}H_{17}O_4P$. Ethyl (2-methoxycarbonylethyl)-phenylphosphinate, preparation, properties, 805.

$C_{12}H_{17}O_5N$. 1) Acid oxalate of 4-anilinobutan-1-ol, preparation, 344.
2) 4-anilinobut-1-yl hydrogen oxalate, preparation, 343.

$C_{12}H_{19}O_2P$. Hexyl hydrogen phenylphosphonite, preparation, addition to methyl methacrylate, 805.

$C_{12}H_{19}O_3N_3$. 1) Semicarbazone of keto-acid formed by condensing 2-methyldihydroresorcinol with but-1-en-3-one, 314.
2) Semicarbazone obtained from hydrolytic decomposition products of 1,6-diketo-9-methyl-Δ^5-octalin, 316.

$C_{12}H_{21}ON_3$. Semicarbazone of di-(3-methylcyclobutyl) ketone, 321.

$C_{12}H_{23}O_3P$. 1) Dicyclohexylphosphorous acid, preparation, properties, 724.
2) Dibutyl 2,5-dimethyl-3-cyclohexenylphosphonate, preparation, properties, 817.

$C_{12}H_{23}O_7P$. Diethyl diethoxyphosphinylsuccinate, preparation, properties, 824.

$C_{12}H_{26}O_6As_2$. (Methoxymethyl) ethylene ester of arsenious acid, preparation, properties, 807.

$C_{12}H_{24}O_{10}P_2$. Diethyl bis(dimethoxyphosphinyl)succinate, preparation, properties, 824.

$C_{12}H_{25}O_5P$. 1) Butyl β-diethylphosphoneisobutyrate, preparation, properties, 659.
2) Isobutyl β-diethylphosphoneisobutyrate, preparation, properties, 659.

$C_{12}H_{26}O_2S$. 1) β,β'-Dibutoxydiethyl sulfide, properties, 460.
2) α, β-Diisobutoxydiethyl sulfide, properties, 461.

$C_{12}H_{27}SiCl$. Tributylchlorosilane, preparation, properties, 537.

$C_{12}H_{27}O_2P$. 1) Decyl hydrogen ethylphosphonite, preparation, properties, 846.
2) Diisobutyl isobutylphosphonite, preparation, properties, 801.
3) Isobutyl diisobutylphosphinate, preparation, properties, 802.

$C_{12}H_{23}SiO_3$. Triallylcyclohexylsilane, preparation, properties, 537.

12. IV

$C_{12}H_{13}O_4N_3S$. p-Acetamidophenyl-N-methylpyrazolonesulfone, preparation, hydrolysis, 921.

$C_{12}H_{13}O_5N_3S$. p-Carbomethoxyaminophenyl-N-3-methylpyrazolonesulfone, preparation, 920.

$C_{12}H_{17}N_2OCl$. Monohydrochloride of 1-α-pyridyl-2,5-dimethyl-4-piperidone, preparation, 930.

$C_{12}H_{19}O_4PS$. Diethyl 1-furyl-3-oxobutylphosphonothionate, preparation, properties, 828.

$C_{12}H_{22}O_2PCl$. Dicyclohexyl phosphorochloridite, preparation, properties, 725.

$C_{12}H_{26}O_4NP$. β-Dibutylphosphoneisobutyramide, preparation, properties, 658.

$C_{12}H_{27}O_2PS$. Diisobutyl isobutylphosphonothionate, preparation, properties, 801.

$C_{12}H_{27}O_2PS_2$. Product of reaction of P_4S_7 with n-butanol, 666.

$C_{12}H_{27}O_2PSe$. Diisobutyl isobutylphosphonoselenonate, preparation, properties, 801.

$C_{12}H_{27}O_3PS$. Dibutyl 2-ethylmercaptoethylphosphonate, preparation, properties, 816.

$C_{12}H_{27}O_3TiCl$. 1) Tri-isobutoxytitanium chloride, preparation, properties, 83.
2) Tri-n-butoxytitanium chloride, preparation, properties, 83.
3) Tri-β-ethoxyethoxytitanium chloride, preparation, properties, 84.

12. V

$C_{12}H_{15}O_3PCuBr$. Cuprous bromide compound of cyclo hexyl o-phenylene phosphite, preparation, 727.

$C_{12}H_{26}O_2SHgCl_2$. Compound of β,β'-diisobutoxydiethyl sulfide with mercuric chloride, 460.

$C_{12}H_{30}O_6P_2PtI_2$. Product of reaction of potassium iodide with $PtCl_2 \cdot 2P(OC_2H_5)_3$, 741.

12. VII

$C_{12}H_{15}O_3PCuCNS$. Complex compound of benzyl-1-methyltrimethylene phosphite and cuprous thiocyanate, preparation, 733.

$C_{12}H_{33}O_3PPtS_3N_6Cl_2$. Product of reaction of thiourea with $PtCl_2 \cdot 2P(OC_3H_7\text{-}i)_3$, 742.

Group C_{13}

13. I

$C_{13}H_{22}$. 1) Dehydration product of 1,6-dihydroxy-1,6,9-trimethyldecalin, 646.
2) 1,6,9-Trimethyl-Δ-1,6-hexalin, preparation, dehydrogenation, 645.

$C_{13}H_{24}$. Tridecadiene, preparation, properties, oxidation, 952.

$C_{13}H_{28}$. Tetrapropylmethane, preparation, properties, 946.

13. II

$C_{13}H_{16}O_3$. 1-Benzyl-oxyethyl methacrylate, synthesis, properties, 456.

$C_{13}H_{16}O_4$. 1,6-Diketo-9-methyl-5-carboxymethyl-Δ^5-octalin, preparation, 316.

$C_{13}H_{16}O_2$. 1-Ethynyltetrahydro-1-hydroxy-3,7a-dimethyl-5(4H)-indandione, preparation, 431.

$C_{13}H_{18}O_5$. Ketodicarboxylic acid formed by hydrolytic decomposition of product of condensation of 2-methyl-dihydroresorcinol with 5-carbomethoxy-pent-1-en-3-one, 316.

$C_{13}H_{20}O_2$. Tetrahydro-1-hydroxy-3,7a-dimethyl-1-vinyl-6(5H)-indanone, preparation, 432.

$C_{13}H_{20}N_2$. 4-Amino-1-phenyl-2,5-dimethylpiperidine, preparation, properties, action of HCl, 935.

$C_{13}H_{22}O$. 1) Dehydratien product of 1,6-dihydroxy-1,6,9-trimethyldecalin, 646.
2) 6-Hydroxy-1,6,9-trimethyl-Δ'-octalin-preparation, 645.

$C_{13}H_{24}Si$. 1) Methyltri-(methylallyl)silane, preparation, properties, 990.
2) Triallylbutylsilane, preparation, properties, 537.

$C_{13}H_{24}O_2$. 1,6-Dihydroxy-1,6,9-trimethyldecalin, preparation, dehydration, 645.

$C_{13}H_{27}Cl$. Tributylmethyl chloride, preparation, properties, 947.

$C_{13}H_{30}Si$. Silicohydrocarbon, properties, 986.

13. III

$C_{13}H_{11}ON$. Benzanilide, preparation, 535.

$C_{13}H_{11}O_6N_3$. 2-(3',5'-Dinitrobenzoyl)-3,6-endoethyleno-3,6-dihydro-ortho-oxazine, preparation, 358.

$C_{13}H_{13}O_2N$. 1) 2-Benzoyl-3,6-endoethyleno-3,6-dihydro-ortho-oxazine, preparation, 358.
2) β-(β-Naphthyl)-β-alanine, preparation, properties, 126.

$C_{13}H_{13}O_6N_3$ 2-(3',5'-Dinitrobenzoyl)-4,5-dimethyl-3,6-dihydro-ortho-oxazine, preparation, 357.

$C_{13}H_{14}ON_2$. Amide of β-(β-naphthyl)-β-alanine, preparation, 128.

$C_{13}H_{15}ON$. Carbostyril propoxymethyl ether, preparation, hydrolysis, isomerization, 750.

$C_{13}H_{15}O_6N$. Reaction product of monoethyl malonate, piperonal, and ammonia, 639.

$C_{13}H_{16}O_2N_2$. 1-p-Nitroso-2,5-dimethyl-4-piperidone, preparation, hydrolysis, 934.

$C_{13}H_{16}N_4O_4$. 2,4-dinitrophenylhydrazone of 3-acetyl-1-methylcyclobutane, preparation, 320.

$C_{13}H_{17}ON$. 1) N-Crotyl-acet-p-toluidide, preparation, properties, oxidation, 610.
2) 3,6-Dihydro-4,5-dimethyl-2-(p-tolyl)-1,2,2H-oxazine, preparation, 541.
3) 5-Phenyl-2,6-dimethyl-4-piperidone, preparation, formation of hydrochloride, 926.
4) 1-Phenyl-2,5-dimethyl-4-piperidone, preparation, properties, 927.

$C_{13}H_{18}ON_2$. 1) 1-p-Aminophenyl-2,5-dimethyl-4-piperidone, preparation, properties, 935.
2) Oxime of 1-phenyl-2,5-dimethyl-4-piperidone, preparation, reduction, 935.

$C_{13}H_{19}O_4P$. Ethyl (2-methoxycarbonylpropyl)-phenyl phosphinate, preparation, properties, 805.

$C_{13}H_{21}O_2P$. Heptyl hydrogen phenylphosphonite, preparation, 805.

$C_{13}H_{22}N_2Cl_2$. 4-Amino-1-phenyl-2,5-dimethylpiperidine dihydrochloride, preparation, 936.

$C_{13}H_{22}O_2N_6$. Disemicarbazone of tetrahydro-3, 7a-dimethyl-1,5(4H)-indandione, preparation, 430.

$C_{13}H_{25}O_3P$. Dicyclohexyl methyl phosphite, preparation, properties, 726.

$C_{13}H_{27}O_4P$. Butyl (2-butoxycarbonylethyl)-phosphinate, preparation, properties, 806.

$C_{13}H_{29}O_3P$. 1) Dihexyl methylphosphonate, preparation, properties, 791.
2) Decyl ethyl methylphosphonate, preparation, properties, 792.

13. IV

$C_{13}H_{17}PN_4O_7$. 1) 2,4-Dinitrophenylhydrazone of 2,5-dimethyl-3-oxocyclopentylphosphonic acid, preparation, 521.
2) 2,4-Dinitrophenylhydrazone of 1-methyl-3-oxocyclohexylphosphonic acid, preparation, 521.

$C_{13}H_{18}ONCl$. 1) 5-Phenyl-2,6-dimethyl-4-piperidone hydrochloride, preparation, 926.
2) 1-Phenyl-2,5-dimethyl-4-piperidone hydrochloride, preparation, 928.

$C_{13}H_{28}O_4NP$. 1) N,N-Diethyl(dialkoxyphosphinyl) formamide derivative, dipole moments, 781.
2) N,N-Diethyl(dibutoxyphosphinyl) formamide, preparation, properties, 762.

13. VII

$C_{13}H_{17}PN_4O_7C_2H_5OH$. 2,4-Dinitrophenylhydrazone of 1-methyl-3-oxocyclohexylphosphonic acid, preparation, 521.

Group C_{14}

14. I

$C_{14}H_{10}$. Anthracene, relative activities of meso carbon atom in reactions with oxidizing agents, 135.

14. II

$C_{14}H_8Cl_2$. 9,10-Dichloranthracene, relative activities of the meso carbon atom in reactions with oxidizing agents, 135.

$C_{14}H_{12}O_2$. Methyl ester of β-(-naphthyl)-acrylic acid, preparation, 126.

$C_{14}H_{14}O$. Diphenyl acetal, preparation, properties, 960.

$C_{14}H_{22}O_2$. 1-Ethynylhexahydro-5-methoxy-3,7a-dimethyl-1-indanol, preparation, hydrogenation, 433.

$C_{14}H_{24}O_2$. Hexahydro-5-methoxy-3,7a-dimethyl-1-vinyl-1-indanol, preparation, 434.

$C_{14}H_{26}O_2$. Hydrogenation product of 1-ethynyl-1-hexahydro-5-methoxy-3,7a-dimethyl-1-indanol, 433.

$C_{14}H_{26}O_3$. Mono-butyl acetal of tetramethylbutindiol, preparation, hydrolysis, properties, 956.

$C_{14}H_{30}O_4$. Dibutyl acetal of ethylene glycol, preparation, properties, hydrolysis, 623.

$C_{14}H_{30}O_6$. Diethyltriacetal of ethylene glycol, preparation, properties, hydrolysis, 620.

$C_{14}H_{32}Si$. Ethyltributylsilane, preparation, properties, 596.

14. III

$C_{14}H_{12}O_2N_2$. 6-(β-Naphthyl)-dihydrouracil, preparation, properties, 288.

$C_{14}H_{15}O_2N_3$. β-Guanidino-β-(β-naphthyl)-propionic acid, preparation, properties, 290.

$C_{14}H_{14}O_3N_2$. β-Ureido-β-(β-naphthyl)-propionic acid, preparation, properties, 286.

$C_{14}H_{14}N_4O_4$. 2,4-Dinitrophenylhydrazone of hydrocarbon hydration product, 692.

$C_{14}H_{15}O_2N$. 1) Methyl ester of β-(β-naphthyl)-β-alanine, preparation, properties, 128.
2) N-methyl-β-(β-naphthyl)-β-alanine, preparation, properties, 129.

$C_{14}H_{15}O_2N_3$. β-Ureido-β-(β-naphthyl)-propionamide, preparation, 288.

$C_{14}H_{15}O_2P$. Diphenyl ethylphosphonite, preparation, properties, action of sulfur, cuprous iodide, 769.

$C_{14}H_{17}O_3N$. Diacetyl derivative of 4-anilinobut-2-en-1-ol, preparation, oxidation, properties, 342.

$C_{14}H_{19}ON$. 1) 5-Phenyl-1,2,6-trimethyl-4-piperidone, preparation, properties, 926.
2) 1-p-Tolyl-2,5-dimethyl-4-piperidone, preparation, properties, 929.

$C_{14}H_{19}O_2N$. 1-p-Methoxyphenyl-2,5-dimethyl-4-piperidone, preparation, properties, 930.

$C_{14}H_{21}ON_3$. Semicarbazone of 3a, 6, 7, 7a-tetrahydro-1, 3a-dimethyl-3-vinyl-5(4H)-indenone, preparation, 432.

$C_{14}H_{21}O_4P$. Ethyl (2-ethoxycarbonylpropyl)-phenylphosphinate, preparation, properties, 806.

$C_{14}H_{23}O_2N_3$. Semicarbazone of tetrahydro-1-hydroxy-3,7a-dimethyl-1-vinyl-6(5H)-indanone, preparation, 432.

$C_{14}H_{23}O_2P$. Octyl hydrogen phenylphosphonite, preparation, 805.

$C_{14}H_{24}N_2Cl_2$. 4-Methylamino-1-phenyl-2,5-dimethylpiperidine dihydrochloride, preparation, 936.

$C_{14}H_{27}O_3P$. Dicyclohexyl ethyl phosphite, preparation, properties, 726.

$C_{14}H_{27}O_7P$. Dimethyl dibutoxyphosphinylsuccinate, preparation, properties, 823.

$C_{14}H_{29}O_4P$. Butyl (2-butoxycarbonylpropyl)-ethylphosphinate, preparation, properties, 806.

$C_{14}H_{29}O_5P$. Hexyl β-diethylphosphoneisobutyrate, preparation, properties, 659.

$C_{14}H_{30}O_2S$. 1) α,β-Diisoamyloxydiethyl sulfide, properties, 462.
2) β,β'-Diisoamyloxydiethyl sulfide, properties, 462.

$C_{14}H_{30}O_2S_2$. bis(β-Isobutoxyethyl)mercaptal, preparation, properties, 461.

$C_{14}H_{31}O_2P$. Dihexyl ethylphosphonite, preparation, properties, 768.

$C_{14}H_{31}O_3P$. Ethyl hexyl hexylphosphonate, preparation, properties, 793.

$C_{14}H_{31}O_4N$. Reaction product from β-chloroethyl isopropyl acetal and ammonia, 189.

14. IV

$C_{14}H_{12}ON_2S$. 2-Thio-6-(β-naphthyl)-dihydrouracil, preparation, properties, 290.

$C_{14}H_{20}ONCl$. 1-p-Tolyl-2,5-dimethyl-4-piperidone hydrochloride, preparation, 929.

$C_{14}H_{20}O_2NCl$. 1-p-Methoxyphenyl-2,5-dimethyl-4-piperidone hydrochloride, preparation, 929.

$C_{14}H_{22}O_4NP$. p-Toluidine salt of 2,5-dimethyl-3-oxocyclopentylphosphonic acid, preparation, 520.

Group C_{15}

15. II

$C_{15}H_{20}Si$. Phenyltriallylsilane, preparation, properties, 595.

$C_{15}H_{22}O$. 1-(Cyclohex-1',3'-dienyl)-4-methyl-3-isopropylpent-1-yn-3-ol, preparation, properties, 692.

$C_{15}H_{22}O_5$. Dimethyl ester of 1,6-diketo-9-methyl-

5-carboxymethyl-Δ^{5}-octalin, preparation, hydrolysis, ozonation, 316.

$C_{15}H_{32}Si$. Allyltributylsilane, preparation, properties, 537; 595.

15. III

$C_{15}H_{11}O_2N$. N-Benzylisatin, preparation, 445.

$C_{15}H_{16}ON_2$. 4-Oxo-6-(β-naphthyl)-2-methyl-3,4,5,6-tetrahydropyrimidine, preparation, properties, 290.

$C_{15}H_{14}O_2N_2$. 6-(β-Naphthyl)-1-methyldihydrouracil, preparation, properties, 289.

$C_{15}H_{15}O_3N$. N-Acetyl-β-(β-naphthyl)-β-alanine, preparation, properties, 128.

$C_{15}H_{16}O_3N_2$. β-(N_1-methylureido)-β-(β-naphthyl)-propionic acid, preparation, 288.

$C_{15}H_{17}O_2N$. n-Butyl-α-naphthylurethane, preparation, 343.

$C_{15}H_{19}O_3N$. Diacetyl derivative of 4-p-tolylaminobut-2-en-1-ol, preparation, properties, oxidation, 609.

$C_{15}H_{22}ON_2$. 4-Acetamido-1-phenyl-2,5-dimethylpiperidine, preparation, 936.

$C_{15}H_{25}O_2P$. Nonyl hydrogen phenylphosphonite, preparation, 805.

$C_{15}H_{23}O_3N$. Dibenzoyl derivative of 4-p-tolylaminobut-2-en-1-ol, preparation, 609.

$C_{15}H_{23}O_4P$. 1) Ethyl (2-propoxycarbonylpropyl)-phenylphosphinate, preparation, properties, 806.
2) Isobutyl (2-methoxycarbonylpropyl) phenylphosphinate, preparation, properties, 806.

$C_{15}H_{29}O_3P$. Dibutyl 2-methyl-3-cyclohexenylphosphonate, preparation, properties, 816.

$C_{15}H_{31}O_5P$. Heptyl β-diethylphosphoneisobutyrate, preparation, properties, 659.

15. IV

$C_{15}H_{15}O_4N_3S$. p-Carbomethoxyaminophenylsulfonylhydrazone of benzaldehyde, preparation, 920.

$C_{15}H_{22}O_2NCl$. 1-p-Ethoxyphenyl-2,5-dimethyl-4-piperidone hydrochloride, preparation, 930.

$C_{15}H_{32}O_4NP$. 1) N,N-diethyl(dialkoxyphosphinyl) formamide derivative, dipole moments, 781.
2) N,N-Diethyl(diisopentyloxyphosphinyl)formamide, preparation, properties, 763.

$C_{15}H_{33}O_3TiCl$. Tri-isoamyloxy-titanium chloride, preparation, properties, 82.

15. V

$C_{15}H_{25}N_2O_2PS$. Phenyl hydrazone of diethyl 1-methyl-3-oxobutyl-phosphonothionate, preparation, 827.

Group C_{16}

16. II

$C_{16}H_{18}Si$. Diphenylallylmethylsilane, preparation, properties, 595.

$C_{16}H_{24}O_7$. Tricarboxylic acid obtained from condensation of 1-carbomethoxy-1-methylcyclohex-2-en-4-one with malonic ester, 647.

$C_{16}H_{28}Si$. Tetra-(methylallyl)-silane, preparation, properties, 990.

$C_{16}H_{28}O_6$. Cyclic ester of triethylene glycol with sebacic acid, preparation, 779.

$C_{16}H_{30}O_4$. Diethylacetal of tetramethylbutindiol, preparation, properties, hydrolysis, 957.

16. III

$C_{16}H_{16}O_3N_2$. 4-Piperonyl-2-imidazolidone, preparation, 853.

$C_{16}H_{13}NO$. Benzylcarbostyril, preparation, hydrolysis, isomerization, 751.

$C_{16}H_{13}O_2N$. (p-Tolylmethyl)-isatin, preparation, 446.

$C_{16}H_{21}O_3N$. Diacetyl derivative of 2,3-dimethyl-4-phenylamino-2-buten-1-ol, preparation, properties, 541.

$C_{16}H_{13}O_4N_3$. 3-Benzoyl-4-(m-nitrophenyl)-2-imidazolidone, preparation, action of KOH, 852.

$C_{16}H_{14}O_2N_2$. 3-Benzoyl-4-phenyl-2-imidazolidone, preparation, hydrolysis, 850.

$C_{16}H_{14}O_5N_2$. N-Benzoyl-β-(m-nitrophenyl)-β-alanine, preparation, formation of ethyl ester, hydrazide, azide, 850.

$C_{16}H_{15}ON$. 3,6-Dihydro-2,6 (or 2,3)-diphenyl-1,2,2H-oxazine, preparation, 541.

$C_{16}H_{16}O_4N_4$. N-Benzoyl-β-(m-nitrophenyl)-β-alanine, hydrazide, preparation, properties, 851.

$C_{16}H_{17}O_2N_3$. N-benzoyl-β-phenyl-β-alanine, hydrazide, preparation, properties, 848.

$C_{16}H_{18}O_2N_4$. β-(m-Aminophenyl)-N-benzoyl-β-alanine hydrazide, preparation, 851.

$C_{16}H_{19}O_3N$. Diacetyl derivative of 4-anilino-cyclohex-2-en-ol, preparation, 615.

$C_{16}H_{19}O_3P$. bis(β-Phenylethyl)-phosphorous acid,

preparation, properties,487.

$C_{16}H_{20}ON_2$. β-Benzamido-β-cyclohexylpropionamide, preparation, properties, 297.

$C_{16}H_{20}O_2N_2$. 1-Benzoyl-5-cyclohexylglyoxalidone, preparation, 298.

$C_{16}H_{21}ON$. 1-Phenyl-2-methyl-4-ketodecahydroquinoline, preparation, 931.

$C_{16}H_{21}O_3N$. 1) β-Benzamido-β-cyclohexylpropionic acid, preparation, properties, 296.
2) Diacetyl derivative of 4-anilinocyclohexan-1-ol, preparation, 616.

$C_{16}H_{28}N_2O_4$. Product of reaction of vinylcaprolactam with hydrogen peroxide, 631.

$C_{16}H_{31}O_3P$. Butyl dicyclohexyl phosphite, preparation, properties, 727.

$C_{16}H_{31}O_7P$. Diethyl dibutoxyphosphinyl-succinate, preparation,properties, 824.

$C_{16}H_{32}O_{10}P_2$ Diethyl bis(diethoxyphosphinyl) succinate, preparation, properties, 824.

$C_{16}H_{33}O_5P$. Octyl β-diethylphosphoneisobutyrate, preparation, properties, 659.

$C_{16}H_{34}O_2S_2$. bis(β-Isoamyloxyethyl) mercaptal, preparation, properties, 463.

$C_{16}H_{35}O_4N$. Bis-α-(isobutoxyethyl) ether of diethanolamine, preparation, properties, 190.

16. IV

$C_{16}H_{14}NClO_4$. N-Phenylquinaldine perchlorate, preparation, properties, 353.

$C_{16}H_{18}O_2N_3Cl$. Hydrochloride of N-benzoyl-β-phenyl-β-alanine hydrazide, preparation, properties, preparation of azide, 849.

$C_{16}H_{22}ONCl$. 1-Phenyl-2-methyl-4-keto-decahydroquinoline hydrochloride, preparation, 931.

16. V

$C_{16}H_{27}O_2N_2PS$. Phenylhydrazone of diethyl 1,1-dimethyl-3-oxobutylphosphonothionate, preparation, 828.

Group C_{17}

17. I

$C_{17}H_{36}$. Tetrabutylmethane, preparation, properties, 947.

17. II

$C_{17}H_{17}N$. Benzoyl derivative of N-2-butenylaniline, preparation, hydrolysis, 534.

$C_{17}H_{20}O_4$. Tricyclic fluorenedicarboxylic acid anhydride, preparation, hydrolysis, 433.

$C_{17}H_{22}O_5$. 1,2,3,4b,5,6,7,8,8a,9a-Decahydro-4b,9-dimethyl-6-oxofluorene-1,2-dicarboxylic acid, preparation, 433.

C17. III

$C_{17}H_{16}O_4N_2$. 3-Benzoyl-4-piperonyl-2-imidazolidone, preparation, hydrolysis, 853.

$C_{17}H_{15}ON$. (p-Tolylmethyl)carbostyril, preparation, hydrolysis, isomerization, 751.

$C_{17}H_{17}ON$. 1) N-2-butenylbenzanilide, preparation, hydrolysis, 528.
2) 3,6-Dihydro-2-phenyl-6(or 3)-(o-tolyl)-1,2,2H-oxazine, preparation, 541.
3) 3,6-Dihydro-2-phenyl-6(or 3)-(p-tolyl)-1,2,2H-oxazine, preparation, 541.

$C_{17}H_{17}O_4N_3$. N-Benzoyl-β-piperonyl-β-alanine hydrazide, preparation, 852.

$C_{17}H_{19}ON$. N-n-butylbenzanilide, preparation, 344.

$C_{17}H_{23}O_2N$. 1-p-Methoxyphenyl-2-methyl-4-keto-decahydroquinoline, preparation, 931.

$C_{17}H_{27}O_4P$. Hexyl (2-methoxycarbonylpropyl)-phenylphosphinate, preparation, properties, 806.

$C_{17}H_{35}O_5P$. 1) Methyl-β-dihexylphosphoneisobutyrate, preparation, properties, 658.
2) Nonyl β-diethylphosphoneisobutyrate, preparation, properties, 660.

$C_{17}H_{37}O_3P$. Dioctyl methylphosphonate, preparation, properties, 791.

17. IV

$C_{17}H_{18}NClO_4$. N-Phenyl-6-methylquinaldine perchlorate, preparation, 353.

$C_{17}H_{24}O_2NCl$. 1-p-Methoxyphenyl-2-methyl-4-keto-decahydroquinoline hydrochloride, preparation, action of ammonia, 931.

$C_{17}H_{36}O_4NP$. 1) N,N-Diethyl(dihexylphosphinyl) formamide, preparation, properties, 763.
2) N,N-Diethyl(dialkoxyphosphinyl)formamide derivative, dipole moments, 781.

Group C_{18}

18.II

$C_{18}H_{24}O_4$. Tricyclic fluorenecarboxylic anhydride obtained by condensation of 3a,4,5,6,7,7a-hexahydro-6-methoxy-1,3a-dimethyl-3-vinylindene with maleic anhydride, 434.

$C_{18}H_{26}O_5$. 1,2,3,4b,5,6,7,8,8a,9a-Decahydro-7-methoxy-4b,9-dimethylfluorene-1,2-dicarboxylic acid, preparation, 434.

$C_{18}H_{28}O_2$. Compound obtained by reaction of 1-decalone with 1-acetyl-1-cylcohexene, 425.

$C_{18}H_{34}O_3$. Monooctyl acetal of tetramethylbutindiol, preparation, properties, hydrolysis, 957.

18. III

$C_{18}H_{19}O_3N$. Ethyl ester of N-benzoyl-β-phenyl-β-alanine, preparation, 640.

$C_{18}H_{18}O_5N_2$. Ethyl ester of N-benzoyl-β-(m-nitrophenyl)-β-alanine, preparation, 851.

$C_{18}H_{18}O_8N_4$. Picrate of 4-anilinocyclohex-2-en-1-ol, preparation, 615.

$C_{18}H_{19}ON$. N-Crotyl-benz-p-toluidide, preparation, properties, 610.

$C_{18}H_{20}O_3N_2$. Ethyl ester of 2-benzamido-2-phenylethylcarbamic acid, preparation, 850.

$C_{18}H_{25}ON$. 1,2,3,4,4a,6a,7,8,9,10-decahydro-6-phenyl-6H-dibenz[c, e]-o-oxazine, preparation, 541.

$C_{18}H_{33}O_3P$. Tricyclohexyl phosphite, preparation, 725.

$C_{18}H_{39}O_2P$. Dioctyl ethylphosphonite, preparation, properties, 768.

$C_{18}H_{39}O_3P$. 1) Dinonylphosphorous acid, preparation, properties, 487.

2) Ethyl octyl octylphosphonate, preparation, properties, 793.

3) Dihexyl hexylphosphonate, preparation, properties, 793.

$C_{18}H_{40}O_6P_2$. Tetrabutyl 1,2-ethyldiphosphonate preparation, properties, 814.

18. IV

$C_{18}H_{18}NClO_4$. N-(p-Tolyl)-6-methylquinaldine perchlorate, preparation, 353.

$C_{18}H_{39}O_3TiCl$. Tri-n-hexyloxytitanium chloride, preparation, properties, 84.

18. V

$C_{18}H_{15}O_3PAuCl$. Complex compound of triphenyl phosphite with aurous chloride, preparation, 734.

$C_{18}H_{15}O_3PAuCl$. Complex compound of triphenyl phosphite with aurous chloride, preparation, 734.

$C_{18}H_{30}O_6P_2PtCl_2$. Product of reaction of triphenyl phosphite with platinous chloride, 740.

$C_{18}H_{42}O_6P_2PtCl_2$. Product of reaction of platinous chloride with triisopropyl phosphite, 740.

$C_{18}H_{42}O_6P_2PtI_2$. Product of reaction of potassium iodide with $PtCl_2 \cdot 2P(OC_3H_7\text{-}i)_3$, 741.

Group C_{19}

19. I

$C_{19}H_{38}$. 7-Hexyltridec-6-ene, preparation, properties, 947.

19. II

$C_{19}H_{20}O_3$. Tetracyclic triketone obtained by condensation of 3a,4,7,7a-tetrahydro-1,3a-dimethyl-3-vinyl-6(5H)-indenone with p-quinone, 432.

$C_{19}H_{22}O_4$. Diethylacetal of ethylene glycol, preparation, hydrolysis, properties, 620.

$C_{19}H_{22}O_5$. β-Hydroxyethyl-β-ethoxyethylideneoxyethylacetal, preparation, properties, 620.

$C_{19}H_{24}O_2$. Tetracyclic diketone obtained by condensation of 3a,4,7,7a-tetrahydro-1,3a-dimethyl-3-vinyl-6(5H)-indenone with 2-methyl-2-cyclopenten-1-one, 431.

$C_{19}H_{28}O_2$. 1) Compound obtained by reaction of 3a,4,7,7a-tetrahydro-3, 7a-dimethyl-1-indanone with 1-acetyl-1-cyclohexene, 425.

2) Compound obtained by the reaction of 8a-methyl-1-octalone with 1-acetyl-1-cyclohexene, 425.

3) Hydrogenation product of tetracyclic diketone obtained by condensation of 3a,4,7,7a-tetrahydro-1,3a-dimethyl-3-vinyl-6(5H)-indenone with 2-methyl-2-cyclopenten-1-one, 431.

$C_{19}H_{22}Si$. Triallyl-α-naphthylsilane, preparation, 537.

$C_{19}H_{39}Cl$. Tri-n-hexylmethyl chloride, preparation, properties, 947.

$C_{19}H_{40}O$. Tri-n-hexylcarbinol, preparation, 947.

$C_{19}H_{42}Si$. Silicohydrocarbon, properties, 986.

19. III

$C_{19}H_{19}ON$. Benzoyl derivative of 3-anilinocyclohex-1-ene, preparation, 616.

$C_{19}H_{19}O_5N$. Ethyl ester of N-benzoyl-β-piperonyl-β-alanine, preparation, formation of hydrazide, azide, 852.

$C_{19}H_{20}O_8N_4$. Picrate of 1-phenyl-2,5-dimethyl-4-piperidone, preparation, 928.

$C_{19}H_{27}ON$. 1,2,3,4,4a,6a,7,8,9,10-Decahydro-6-(p-tolyl)-6H-dibenz [c,e]-o-oxazine, preparation, 542.

$C_{19}H_{29}O_3P$. Benzyl dicyclohexyl phosphite, preparation, properties, 727.

$C_{19}H_{39}O_5P$. Methyl β-diheptylphosphoneisobutyrate, preparation, 659.

19. IV.

$C_{19}H_{12}O_3Na_2P$. Sodium salt of 7-benz[a]anthracenemethane phosphonic acid, preparation, 132.

$C_{19}H_{19}O_5N_3S$. Hydrazone of acetoacetic ester derived from the hydrazide of p-acetaminobenzenesulfonic acid, preparation, 921.

$C_{19}H_{21}O_6N_2S$. Product of reaction of methyl p-carbomethoxybenzenesulfonate and phenylmethylpyrazolone, 920.

$C_{19}H_{22}N_5O_4Cl$. Hydrochloride of dinitrophenylhydrazone of 1-phenyl-2,5-dimethyl-4-piperidone, preparation, 929.

19. V

$C_{19}H_{20}O_4N_3SNa$. Sodium 4-(2,5-dimethyl-4-ketopiperidino)-azobenzene-4'-sulfonate, preparation, 935.

Group C_{20}

20. II

$C_{20}H_{26}O_3$. Tetracyclic diketone obtained by condensation of 3a, 4,5,6,7,7a-hexahydro-6-methoxy-1,3a-dimethyl-3-vinylindene with p-quinone, 434.

$C_{20}H_{28}O_2$. Tetracyclic diketone obtained by condensation of 3a,4,7,7a-tetrahydro-1,3a-dimethyl-3-vinyl-6(5H)-indenone with 2-methyl-2-cyclohexen-1-one, 431.

$C_{20}H_{32}O_2$. Hydrogenation product of tetracyclic diketone obtained by condensation of 3a,4,7,7a-tetrahydro-1,3a-dimethyl-3-vinyl-6(5H)-indenone with 2-methyl-2-cyclohexen-1-one, 431.

$C_{20}H_{38}O_4$. Dibutyl acetal of tetramethylbutindiol, preparation, properties, hydrolysis, 956.

20. III

$C_{20}H_{16}O_2N_2$. 3-Phenyl-6-(β-naphthyl)-dihydrouracil, preparation, properties, 289.

$C_{20}H_{17}O_3N$. N-Benzoyl-β-(β-naphthyl)-β-alanine, preparation, properties, 128.

$C_{20}H_{18}O_3N_2$. β-(ω-Phenylureido)-β-(β-naphthyl)-propionic acid, preparation, properties, 288.

$C_{20}H_{22}ON_2$. 1-p-Benzylideneaminophenyl-2,5-dimethyl-4-piperidone, preparation, 935.

$C_{20}H_{22}O_8N_4$. Picrate of 5-phenyl-1,2,6-trimethyl-4-piperidone, preparation, 927.

$C_{20}H_{24}O_9N_4$. Picrate of β-anilinopropyl β-methoxyisopropyl ketone, preparation, 928.

$C_{20}H_{43}O_3P$. Didecylphosphorous acid, preparation, properties, 487.

$C_{20}H_{44}SiO$. Ethoxytrihexylsilane, preparation, properties, 948.

20. IV

$C_{20}H_{16}NClO_4$. N-α-Naphthylquinaldine perchlorate, preparation, 354.

$C_{20}H_{23}ON_2P$. 12-Methyl-7-benz[a]-anthracenemethanephosphonic acid, preparation, 132.

$C_{20}H_{24}O_5N_5Cl$. Dinitrophenylhydrazone of 1-p-methoxy-2,5-dimethyl-4-piperidone, preparation, 930.

Group C_{21}

21. II

$C_{21}H_{18}O$ 3,3-Diphenyl-1-(cyclohexa-1'-3'-dienyl)-prop-1-yn-3-ol, preparation, properties, 692.

$C_{21}H_{32}O_2$. Tetracyclic ketone obtained by condensation of 3a,4,5,6,7,7a-hexahydro-6-methoxy-1,3a-dimethyl-3-vinylindene with 2-methyl-2-cyclohexen-1-one, 434.

21. III

$C_{21}H_{18}NI$. 1) N-(α-Naphthyl)-6-methylquinaldine iodide, preparation, 353.

2) N-(o-Tolyl)-5,6-benzoquinaldine iodide, preparation, 354.

$C_{21}H_{20}O_2N_2$. Anilide of N-acetyl-β-(β-naphthyl)-β-alanine, preparation, properties, 129.

$C_{21}H_{20}O_3N_2$. Methyl-β-(ω-phenylureido)-β-(β-naphthyl)-2-propionate, preparation, properties, 289.

$C_{21}H_{23}O_8N_5$. Monopicrate of 1-α-pyridyl-2-methyl-4-ketodecahydroquinoline, preparation, 931.

$C_{21}H_{24}O_8N_4$. 5-Phenyl-2,6-dimethyl-1-ethyl-4-piperidone, preparation, 927.

$C_{21}H_{28}O_3N_6$. Disemicarbazone of tetracyclic triketone obtained by condensation of 3a,4,7,7a-tetrahydro-1,3a-dimethyl-3-vinyl-6(5H)-indenone with p-quinone, 432.

$C_{21}H_{32}O_2N_6$. Disemicarbazone obtained from tetracyclic diketone from condensation of 3a,4,7,7a-tetrahydro-1,3a-dimethyl-3-vinyl-6(5H)-indenone with 2-methyl-2-cyclopenten-1-one, 431.

$C_{21}H_{43}O_5P$. Methyl-β-diocytlphosphoneisobutyrate, preparation, properties, 659.

$C_{21}H_{45}O_3P$. Didecyl methylphosphonate, preparation, properties, 792.

$C_{21}H_{45}O_6N$. Reaction product from β-chloroethylisopropyl acetal and ammonia, 190.

21. IV

$C_{21}H_{18}NClO_4$. N-(o-Tolyl)-7,8-benzoquinaldine perchlorate, preparation, 354.

$C_{21}H_{19}PS_2O$. Reaction product of ethylene-o-methyl phosphorodithioite and triphenylmethyl bromide, 440.

Group C_{22}

22. III

$C_{22}H_{21}O_3P$. Product of reaction of trimethylene phosphite and bromotriphenylmethane, 710.

22. IV

$C_{22}H_{22}O_3PBr$. Product of reaction of bromotriphenylmethane on ethylene methyl phosphite, 701.

Group C_{23}

23. III

$C_{23}H_{23}O_3P$. Ester of glycolphosphorous acid, preparation, 710.

Group C_{24}

24. II

$C_{24}H_{52}Si$. Tetrahexylsilane, preparation, properties, 947.

$C_{24}H_{54}Si_2$. 1,8-Di-(triethylsilyl)-2,4,3,7-tetramethyloctane, preparation, properties, 597.

24. III

$C_{24}H_{18}NI$. N-β-Naphthyl-5,6-benzoquinaldine iodide, preparation, 354.

$C_{24}H_{21}O_3N$. 1) Benzoyl derivative of 4-anilinobut-2-en-1-ol, preparation, 342.

2) Dibenzoyl derivative of 4-phenylamino-2-buten-1-ol, preparation, 527.

$C_{24}H_{51}O_3P$. Dioctyl octylphosphonate, preparation, properties, 794.

$C_{24}H_{51}O_6N$. Tris(α-isobutylethyl) ether of triethanolamine, preparation, properties, 191.

24. IV

$C_{24}H_{16}OBr_4As_2$. Product of reaction of potassium p-bromophenylazocarboxylate with arsenic trichloride, 914.

Group C_{25}

25. III

$C_{25}H_{32}O_5N_4$. 1) 2,4-Dinitrophenylhydrazone of compound obtained by reaction of 8a-methyl-1-octalone with 1-acetyl-1-cyclohexene, 425.

2) 2,4-Dinitrophenylhydrazone of compound obtained by reaction of 3a,4,7,7a-tetrahydro-3,7a-dimethyl-1-indanone with 1-acetyl-1-cyclohexene, 425.

25. IV

$C_{25}H_{28}O_3PBr$. Product of reaction of butyl ethylene phosphite and bromotriphenylmethane, 703.

Group C_{27}

27. III

$C_{27}H_{24}N_4O_5$. 2,4-Dinitrophenylhydrazone of 3,3-diphenyl-1-(cyclohexa-1',3'-dienyl)-prop-1-yn-3-ol, 693.

$C_{27}H_{57}O_3B$. Trinonyl borate, preparation, properties, 778.

$C_{27}H_{57}O_3P$. Dinonyl nonylphosphonate, preparation, properties, 794.

27. IV.

$C_{27}H_{23}N_2ClO_4$. [2-(1-Phenylquinoline)][2-(3-ethylbenzothiazole)]trimethinecyanine perchlorate, preparation, 499.

$C_{27}H_{32}O_3PBr$. Ester of glycolphosphorous acid, preparation, 710.

Group C_{28}

28. II

$C_{28}H_{54}O_3$. Dioctyl acetal of tetramethylbutindiol, preparation, properties, hydrolysis, 957.

28. III

$C_{28}H_{21}ON$. (Triphenylmethyl) carbostyril, preparation, hydrolysis, isomerization, 750.

$C_{28}H_{28}As_2O$. Product of reaction of potassium p-tolylazocarboxylate with arsenic trichloride, 914.

28. IV

$C_{28}H_{25}N_2ClO_4$. [2-(6-Methyl-1-phenylquinoline)]-[2-(3-ethylbenzothiazole)]trimethinecyanine perchlorate, preparation, 501.

Group C_{29}

29. IV

$C_{29}H_{27}N_2ClO_4$. 1) [2-(6-Methyl-1-p-tolylquinoline]-[2-(3-ethylbenzothiazole)]trimethinecyanine perchlorate, preparation, 502.

2) (1-Phenyl quinoline -2)-(1,3,3-trimethylindolenine-2)-trimethinecyanine perchlorate, preparation, 670.

Group C_{30}

30. I

$C_{30}H_{30}$. 1) 1,1,6,6,-Tetraphenylhexane, 994.

2) Product of hydrogenolysis of dibenzhydrylthiophen, 994.

30. III

$C_{30}H_{23}BrS$. Bromodibenzhydrylthiophen, preparation, properties, oxidation, 994.

$C_{30}H_{24}O_2S$. 2,5-Dibenzhydrylthiophen-1,1-oxide, preparation, properties, reduction, bromination, 994.

$C_{30}H_{36}O_8N_8$. Bis(2,4-dinitrophenylhydrazone) of compound obtained by reaction of 1-decalone with 1-acetyl-1-cyclo-hexene, 425.

$C_{30}H_{63}O_3P$. Didecyl decylphosphonate, preparation, properties, 794.

30. IV

$C_{30}H_{22}Br_2O_2S$. Bromination product of 2,5-dibenzhydryl-thiophen-1,1-dioxide, preparation, properties, 995.

$C_{30}H_{29}N_2O_4Cl$. (1-Phenyl-6-methylquinoline-2)-(1,3,3-trimethylindolenine-2)-trimethinecyanine perchlorate, preparation, 670.

Group C_{31}

31. III

$C_{31}H_{26}O_3N_4$. Product of hydrolysis of 3-benzoyl-4-phenyl-2-imidazolidone, 850.

31. IV

$C_{31}H_{25}O_4N_2Cl$. 1) [2-(1-(1-Naphthyl)quinoline)] [2-(3-ethylbenzothiazole)] trimethinecyanine perchlorate, preparation, 502.

2) [3-(4-Phenylbenzo[f] quinoline)] [2-(3-ethylbenzothiazole)]trimethinecyanine perchlorate, preparation, 502.

$C_{31}H_{31}N_2O_4Cl$. (1-p-Tolyl-6-methyl-quinoline-2)-(1,3,3-trimethylindolenine-2)-trimethinecyanine perchlorate, preparation, 670.

Group C_{32}

32. III

$C_{32}H_{27}N_2I$. [2-(6-Methyl-1-(1-naphthyl)quinoline)] [2-(3-ethylbenzothiazole)]-trimethinecyanine iodide, preparation. 502.

$C_{32}H_{67}O_3P$. Dihexadecylphosphorous acid, preparation, 487.

32. IV

$C_{32}H_{27}O_4N_2Cl$. 1) [3-(4-o-Tolylbenzo[f]quinoline)] [2-(3-ethylbenzothiazole)]trimethinecyanine perchlorate, preparation, 503.

2) [2-(1-o-Tolylbenzo[h]quinoline)] [2-(3-ethylbenzothiazole)]trimethinecyanine perchlorate, preparation, 502.

Group C_{33}

33. IV

$C_{33}H_{25}N_2O_4Cl$. Bis-2-(1-Phenylquinoline)-trimethinecyanine perchlorate, preparation, 494.

$C_{33}H_{29}O_4N_2Cl$. 1) (1-α-Naphthylquinoline-2)-(1,3,3-trimethylindolenine-2)-trimethinecyanine perchlorate, preparation, 671.

2) (1-Phenyl-5,6-benzoquinoline-2)-(1,3,3-trimethylindolenine-2)-trimethinecyanine perchlorate, preparation, 670.

$C_{33}H_{33}N_2O_4Cl$. [Bis-2-(6-methyl-1-p-tolylquinoline)]-β-methyltrimethinecyanine perchlorate, preparation, 495.

Group C_{34}

34. IV

$C_{34}H_{27}N_2O_4Cl$. [Bis-2-(1-phenylquinoline)]-β-methyl-trimethinecyanine perchlorate, preparation, 494.

$C_{34}H_{31}O_4N_2Cl$. 1) (1-α-Naphthyl-6-methylquinoline-2)-(1,3,3-trimethylindolenine-2)-trimethinecyanine perchlorate, preparation, 670.

2) (1-o-Tolyl-7,8-benzoquinoline-2)-(1,3,3-trimethylindolenine-2)-trimethinecyanine perchlorate, preparation, 670.

3) (1-p-Tolyl-5,6-benzoquinoline-2)-(1,3,3-trimethylindolenine-2)-trimethinecyanine perchlorate, preparation, 671.

Group C_{35}

35. III

$C_{35}H_{27}N_2I$. [3-(4-(2-Naphthyl)benzo[f]quinoline)] [2-(3-ethylbenzothiazole)]trimethinecyanine iodide, preparation, 503.

35. IV

$C_{35}H_{29}N_2O_4Cl$. Bis-2-(6-methyl-1-phenylquinoline) trimethinecyanine perchlorate, preparation, 495.

Group C_{36}

36. III

$C_{36}H_{78}Si_2O$. Hexahexyldisiloxane, preparation properties, 947.

36. V.

$C_{36}H_{30}O_6P_2PtCl_2$. Product of reaction of triphenyl phosphite with platinous chloride, 741.

$C_{36}H_{66}O_6P_2CuBr$. Cuprous bromide compound of tricyclohexyl phosphite, preparation, 726.

Group C_{37}

37. III

$C_{37}H_{31}N_2I$. (1-β-Naphthyl-5,6-benzoquinoline-2)-(1,3,3-trimethylindolenine-2)-trimethinecyanine iodide, preparation, 671.

37. IV

$C_{37}H_{33}N_2O_4Cl$. Bis-2-(6-methyl-1-p-tolylquinoline) trimethinecyanine perchlorate, preparation, 495.

Group C_{41}

41. IV

$C_{41}H_{29}O_4N_2Cl$. 1) Bis-2-[1-(-naphthyl)-quinoline] trimethinecyanine perchlorate, preparation, 495.
2) Bis-3-[4-phenylbenzo[f]quinoline] trimethinecyanine perchlorate, preparation, 496.

Group C_{43}

43. III

$C_{43}H_{33}N_2I$. Bis-3-[4-o-Tolylbenzo[f]quinoline] trimethinecyanine iodide, preparation, 496.

43. IV

$C_{43}H_{33}O_4N_2Cl$. 1) Bis-2-[6-Methyl-1-(1-naphthyl)-quinoline]trimethinecyanine perchlorate, prep-preparation, 495.
2) Bis-2-[1-o-tolylbenzo[h]quinoline] trimethinecyanine perchlorate, preparation, 496.

Group C_{44}

44. IV

$C_{44}H_{35}N_2O_4Cl$. [Bis-2-(6-methyl-1-(naphthyl)quinoline)]-β-methyltrimethinecyanine perchlorate, preparation, 495.

Group C_{48}

48. III

$C_{48}H_{99}O_3B$. Trihexadecyl borate, preparation, 483.

$C_{48}H_{99}O_3P$. Trihexadecyl phosphite, preparation, 483.

$C_{48}H_{102}OSi_2$. Hexaoctyldisiloxane, preparation, properties, 948.

Group C_{49}

49. III

$C_{49}H_{33}N_2I$. Bis-3-[4-(2-naphthyl)benzo[f]quinoline] trimethinecyanine iodide, preparation, 496.

NINETY YEARS OF A. M. BUTLEROV'S THEORY OF CHEMICAL STRUCTURE [1]

On September 19th 1861, 90 years ago, at a congress of German naturalists and medical men at Speyer in Germany, a young Russian chemist, Butlerov, read a paper entitled "The Chemical Structure of Substances". This paper marked the beginning of a new phase in chemical science and was a turning point in the development of theoretical concepts in organic chemistry. To me has fallen the great honor of delivering a discourse on the subject of this outstanding event in the history of chemistry.

Thinking over the question of how best to demonstrate the great significance of Butlerov' scientific feat, I came to the conclusion that I ought, as far as my time and knowledge permit, to unfold before you a picture of the theoretical views, particularly those within the realm of organic chemistry, which were dominant in the first and beginning of the second half of the nineteenth century among West European chemists, and, on this background, to portray the numerous obstacles and difficulties, and later struggle, which Butlerov had to withstand and overcome, before his brilliant theory of the structure of organic compounds obtained the rights of citizenship and became embodied in science.

At the beginning of the last century, the electrochemical theory of Davy and Berzelius held sway among chemists everywhere, and it may certainly be considered that the electrochemical theory embraced all the types of chemical compound known at that time. In Berzelius's opinion, every chemical compound could be imagined to consist of two oppositely charged parts, and, in particular, in such typical cases as the alkali salts of strong acids, there were to be distinguished in the make-up of the compound a negatively charged part, or acid, such as SO_3 (by an acid Berzelius understood what we should now call an acid anhydride), and a positively charged base, such as K_2O. On Berzelius's theory, an acid must contain oxygen, which was then regarded as the most electronegative element. However, already in 1810, Davy failed to detect oxygen in the composition of halogens, which, nevertheless, formed real salts.

A powerful blow was dealt to the electrochemical theory of Berzelius by the work of the French chemist Baptiste Dumas, who in 1834 discovered that in organic compounds, particularly in organic acids, such as acetic acid, one, two, or three proportions of electropositive hydrogen could be replaced by one, two, or three proportions of electronegative chlorine, without essential change in the character of the compound. This phenomenon received the name of metalepsy (i.e., ·

---

[1] Paper read at a general meeting of Division of Chemical Sciences held on the 26th September, 1951, in celebration of the completion of ninety years since A. M. Butlerov's paper on the "Chemical Structure of Substances".

substitution – Translator). At the same time, this reaction served Dumas as a starting point for the creation of the so-called theory of types. As is well known, Dumas distinguished chemical types and mechanical types. It may be noted that Dumas' right to priority for the discovery of the metalepsy reaction was disputed by the French chemist Laurent.

It is appropriate here to draw your attention to the difficulty with which new facts and new views become accepted in science and to the obstinacy with which supporters of the old views, in this case the eminent Swedish chemist Berzelius, defended their scientific theories and convictions. For a long time, Berzelius, in spite of the evidence, resolutely denied the resemblance in type between acetic and trichloroacetic acids, pointing out that with respect to their physical properties these compounds do not resemble one another in the slightest degree. To this, as it seemed to Berzelius, substantial objection Dumas replied in an article in which, among other things, he wrote: "I have known for a long time that replacement of hydrogen in a volatile compound by chlorine makes the substance specifically heavier, less volatile, and possessed of a denser vapor, it is clear therefore that Berzelius's objections are not relevant to the view I have expressed".

Also, Dumas wrote in his article: "I have observed a very remarkable reaction when any alkali acts on trichloroacetic acid: the acid breaks down into two bodies, carbonic acid, which unites with the alkali, and free chloroform. . . . I was convinced and even predicted in my memoir that acetic acid would be capable of an analogous reaction, i.e., that under the action of excess alkali it would be converted into carbonic acid and a hydrocarbon of formula C_4H_8" (in modern language CH_4, or methane – A.E.A.). "This means," Dumas remarks further, "that acetic acid and trichloroacetic acid have analogous properties. . . . and belong to the same organic type". 1)

Extending the concept of substitution, Dumas considered it probable that hydrogen in organic compounds could be replaced not only by chlorine or other elements, but also by complex groups, i.e., radicals, which in these cases play, as it were, the part of actual elements. Later, Dumas came to still wider conclusions.

"Until now," wrote Dumas, "I have argued as if the substitution law could be actually applied only to the replacement of hydrogen, which was indeed the first to be observed. . . ., but it sould be noted," Dumas writes further, "that also carbon . . . and consequently all elements in an organic compound may be successively displaced and replaced by others".

It must be remarked here that this hyperbolical generalization of Dumas was at the time subjected to harsh and even humorous criticism (I am thinking here of Wöhler's well known letter), but the very fact that some elements may be replaced by others served as a fresh starting point in the development of theoretical ideas in chemistry. For the further development of theoretical ideas in chemistry, particularly in organic chemistry, science is indebted to the French chemists Gerhardt and Laurent. In 1841, Gerhardt obtained the chair of organic chemistry at Montpelier, and, faced with the task of expounding organic chemistry to a student audience, he must have met with all those difficulties that were bound to present themselves to every teaching chemist at that period in the evolution of organic chemistry, when, as a result of the rapid development in pre-

---

1) Comptes rend. 9 (1839); Comptes rend. 10, 149-178 (1840).

parative synthetic chemistry and of the multitude of new compounds that had been prepared and of new facts that had been discovered, there was a mass of accumulated material that could not be brought within the scope of the prevailing dualistic theory of Berzelius.

The basic problems and aims of research chemists were formulated by Gerhardt in the following words: 'Chemistry concerns itself with the changes of matter; its attention is focused on transformations - it is here that its essential nature lies; it investigates the origin of substances; it records their past and indicates their future; it keeps track of a substance through its various phases until its return to its original state - I do not say 'until its end,'" remarks Gerhardt, "because it has no end. Matter is not destructible, it only changes." (Introduction a la chimie unitaire.)

Gerhardt's great service in the development of theoretical chemistry was the delimiting of the concepts of atom, particle (i.e., molecule - Translator), combining weight, and equivalent. Before Gerhardt's time, chemists had attributed atomic weights to the various elements in rather arbitrary fashion; thus, for oxygen some assumed the atomic weight to be 8, while others assumed it to be 16, atomic weights of 6 and 12 were quoted for carbon, and so on. This confusion was, of course, reflected also in the representation of the formulas of compounds. Gerhardt shared the honor of establishing these most important concepts of chemistry with his friend and supporter Laurent, who must be given the credit for the important idea of taking the volume occupied by a definite amount of a substance in the gas or vapor state as the unit for comparison, following the Avogadro-Ampere hypothesis.

When discussing the establishment of the distinction between the concepts of atom, particle, and equivalent, chemical historians nearly always mention the names of these two French chemists together. It is necessary to add that their work of reforming the whole of chemistry had also its weak aspects, particularly in connection with the determination of the atomic weights of the alkali metals, silver, etc.

The impossibility, with the experimental technique existing at the time, of comparing in the vapor state the volumes of alkali metal or silver compounds with the volumes of compounds of other elements led Gerhardt and Laurent to propose incorrect values for the atomic weights of many elements. This circumstance greatly undermined the faith of chemists in the usefulness of the reform proposed by Gerhardt and Laurent. Later, the above-mentioned difficulties were overcome by the Italian chemist Cannizzaro, who, in the estimation of the atomic weights of the metals, made use of vapor density determinations on certain of their volatile compounds and also of the law of Dulong and Petit.

At an international congress of chemists at Karlsruhe in September 1860, i.e., a year before Butlerov read his paper at Speyer, a communication was made by Cannizzaro, and a resolution was then passed in which principles were laid down for the delimitation of the concepts of atom, particle, and equivalent. The atomic weights proposed by Cannizzaro for the elements were accepted by the great majority of chemists and have been firmly embodied in chemical science from that time on.

The distinction between the concepts of atom and particle established by Gerhardt and Laurent and the replacement of a four-volume formula by a two-volume formula made it possible for these reformers to alter the formulas of an enormous number of substances and, on the basis of the substitution phenomena discovered by Dumas, to declaim energetically against the dualistic concepts of Berzelius. The subsequent application by Gerhardt of the new particle concept led him to the creation of the so-called unitary system or theory.

The unitary system and the new particle weights made it impossible to apply Berzelius's dualistic formulas to such compounds as nitric acid, the caustic alkalis, and many others. Radicals, which on earlier views could exist as separate particles (compounds), were represented according to the new views as groups of atoms, which could go from one compound to another, or could replace individual elements.

The phenomenon of substitution and the new concept of radicals enabled Gerhardt, and at the same time Williamson, to regard complex compounds as derivatives of simpler ones. From this arose the so-called theory of types, which aided the development of synthetic organic chemistry to an extraordinary extent.

May I draw your attention to yet another chemical phenomenon - that which has come to be called isomerism. At the beginning of the nineteenth century, even such great thinkers as Berzelius supposed that the properties of chemical substances were entirely determined by their compositions. Hence, when in 1824 Liebig and Wohler established the composition of silver fulminate and so the composition of fulminic acid and Wohler showed by exact analysis that cyanic acid has the same composition as the fulminic acid of Liebig and Gay-Lussac, this new phenomenon drew very great attention from chemists.

On this occasion Berzelius announced categorically that the cause of the inexplicable coincidence must be sought in inaccurate analysis. At first Liebig held the same view. Later, however, Liebig himself confirmed by analysis the identity in composition of the salts of fulminic and cyanic acis. Very quickly, examples similar to that cited began to multiply, and Berzelius himself acknowledged the existence of a new phenomenon and gave it the name "isomerism." I do not need to go into further details, but will mention only that some time passed before chemists distinguished the phenomenon of isomerism from polymerism and metamerism. The phenomenon of isomerism, as we can now well understand, was bound to play, and in fact did play an important role in the development of the theory of the structure of organic compounds.

The next stage, which brought chemists nearer, first to setting, and then to solving problems on the structure of organic compounds, was the theory of the atomicity of elements (valency). The honor of establishing the concept of valency belongs to the English chemist Frankland, who, already in 1852, established that "no matter what the character of the uniting atoms may be, the combining power of the attracting element is always satisfied by the same number of these atoms."

Although, in the first place, Frankland established this law for inorganic compounds - compounds of nitrogen, phosphorus, antimony, arsenic, and tin - the German chemist Kolbe, on the basis of some very original and unusual considerations, later (1857) extended Frankland's idea to carbon and so acknowledged carbon as a quadrivalent element, admitting, however, at the same time that there are cases of bivalent carbon, e.g., in carbon monoxide, and even cases of tervalency.

Independently of Kolbe, the German chemist Kekule in the same year, 1857, starting from quite different premises, also arrived at the idea of the valency of the elements, and also recognized the quadrivalency or tetrabasicity of the carbon atom, citing as the simplest examples the formulas of methane and carbon tetrachloride; at the same time, he assumed the atomic weight of carbon to be 6. In the next year, 1858, Kekule made the extremely important step of extending the quadrivalency of carbon to compounds containing several carbon atoms and so came to the idea of the chaining together of carbon atoms in these compounds.

In his article "The Constitution and Metamorphoses of Chemical Compounds, and the Chemical Nature of Carbon" Kekule wrote: "For substances containing several carbon atoms, it is necessary to assume that at least some of the atoms are held in combination by the combining power of carbon and that the carbon atoms are themselves united one to another, part of the combining power of one of them being, of course, bound up with the same proportion of the combining power of another." This rule for the chaining together of carbon atoms Kekule extends also to cases in which carbon atoms are combined with other multivalent elements, e.g., in the simplest cases, oxygen and nitrogen.

Here I approach the most important point of my discourse — the question of what chemists of that time thought of the possibility of representing the internal structure of chemical molecules in formulas. It will be obvious that in my short historical sketch I have not said much owing to lack of time and to the wideness of the subject.

The evolution of chemistry, particularly organic, in the period prior to the creation of the theory of chemical structure by Butlerov, proceeded by a more complicated path than that which I have portrayed above. It will be sufficient here to mention the experimental investigations of Williamson on the formation of ethers and the investigations of Gerhardt on the formation of the anhydrides of organic acids, which led to the acceptance of a molecular formula for these substances that was doubled with respect to that previously accepted.

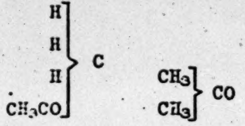
The development of ideas concerning the polybasicity of acids by Berzelius and Liebig and of ideas concerning the polyhydricity of alcohols by Berthelot, Wurtz, and others also played an important role in questions relating to the formulation of the basic concepts of chemistry, which led to the creation of the theory of chemical structure. Berzelius and his followers already used what they called "rational" formulas, which in their opinion expressed the chemical constitution, understood as the presence in complex substances of separate groups of atoms, i.e., radicals.

Gerhardt, as the leader of the new movement in chemistry, had quite a different view on the significance of rational formulas. Gerhardt understood the rational formulas and constitutions of compounds more in terms of their reactivities than their structures. Gerhardt taught, and was himself firmly convinced, that a chemist can have knowledge of a compound only in the course of chemical reactions, i.e., only when it has ceased to exist as such, and a chemist can therefore know and study only the past and the future of a substance. In accordance with what we have just stated, according to Gerhardt, each substance can be assigned as many rational formulas as there are different types of transformation to which it may be subjected.

On the other hand, the theory of types and the theory of substitution often led their adherents to completely wrong conclusions. Thus, for ethane, as a derivative of the hydrogen type, there was the possibility of two isomers: disubstituted hydrogen — dimethyl, and monosubstituted hydrogen — ethyl hydride, and only by the experimental investigations of Schorlemmer was it shown that dimethyl and ethyl hydride are one and the same compound. However, the arbitrary application of the substitution mechanism later led even some of the most eminent chemists to conclusions that had nothing in common with actuality. In this respect, the activity of one of the first-class German chemists, the brilliant experimentalist H. Kolbe, is of particular significance.

Kolbe was a vehement opponent of Gerhardt's new ideas, and in his theoretical conceptions he reverted in many respects to the old views of Berzelius, rejecting however, the unalterability of radicals in the course of chemical change.

Indeed, Kolbe aimed, in a special sense, at arriving at the chemical "constitutions" of compounds, by which he understood the chemical relations of the separate components and not the disposition of the atoms relative to one another in space; in fact, he constantly expressed doubt whether the determination of the disposition of atoms in space would ever become susceptible to study. The incorrect, though in many respects original, theoretical premises of Kolbe, while leading to some successful predictions concerning the existence of hitherto unknown compounds, led very often also to some quite incorrect conclusions. Using the substitution theory, Kolbe successfully predicted the existence of sec.-propyl alcohol and tert.-butyl alcohol. It should be particularly noted that in interpreting substitution phenomena Kolbe made one additional postulate, viz., that in the course of substitution, the "root radical", i.e., in the simplest case, the carbon atom in the compound, is to be distinguished in some way from the carbon atom entering as substituent, or, as Kolbe expresses it, the former "dominates" over the latter. On this basis Kolbe considered that two isomers were possible for acetone, and he denoted the carbon of the "root radical" by heavy type in the formula. According to Kolbe, one isomer of acetone is doubly methylated carbonic acid, and the other is acetylated methane (Fig. 1). The actual facts, of course, are not in accord with these arbitrary speculations of Kolbe.



$$\left.\begin{matrix} H \\ H \\ H \\ CH_3CO \end{matrix}\right\} C \qquad \left.\begin{matrix} CH_3 \\ CH_3 \end{matrix}\right\} CO$$

Fig. 1. Kolbe's formula

It should be mentioned here that Butlerov had a high regard both for the experimental and for the theoretical work of Kolbe, and he considered that only misunderstanding and obstinacy in defending his own views prevented Kolbe from associating himself with the new movement in the science. However, the most interesting matter is the position taken up by Kekule on the burning questions of the day. I have already said that we owe to Kekule the eslishment of the quadrivalency of the carbon atom and of its ability to form carbon chains. Later, Kekule came to acknowledge the necessity of examining the constitutions of compounds, starting from a consideration of the nature of elements, particularly as expressed by their valency. In this way Kekule moved right up to the problem of the structure of organic compounds, but he did not make the decisive step, which speaks very clearly of his attitude in principle to the problem of structure. At the end of his 1858 article Kekule writes: "In conclusion, I consider it necessary to point out that I myself attribute only secondary importance to considerations of this sort (i.e., considerations concerning structure - A.E.A.). . . .".

Subsequently, Kekule remained for a long time under the sway of Gerhardt's ideas, and in his well known textbook of organic chemistry, published 1859-1861, he makes wide use of "rational" formulas in the manner of Gerhardt. The following examples will serve to confirm this: for acetaldehyde Kekule gives four formulas, for acetone - also four formulas, etc. Only by way of exception does Kekule give a few graphical formulas drawn in very ponderous style. These formulas are given in Fig. 2.

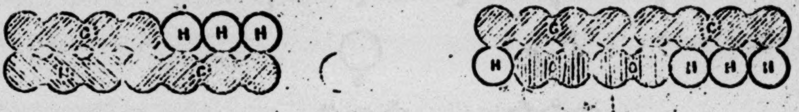
Almost at the same time as the above-mentioned article of Kekule there appeared an article, published in three languages, by the English chemist Couper entitled "A new chemical theory". Couper, independently of Kekule, concluded that investigation into the structures of chemical compounds and into their reactions must start from the concept of the valency of elements.

Assuming valencies of 4 and 2 for carbon, Couper postulates the following two cases:

1) It (i.e., carbon - A.E.A.) unites with the same number of equivalents of hydrogen, chlorine, oxygen, sulfur, etc., which may mutually replace one another, satisfying their combining powers.

2) It (i.e., carbon - A.E.A.) unites with itself. . . On the basis of these theses Couper, in his article, gives a number of structural formulas as examples; in many ways they are reminiscent of modern structural formulas.

Examples of Couper's formulas are given in Fig. 3.



Acetonitrile

Acetic acid

Fig. 2. Kekule's formulas

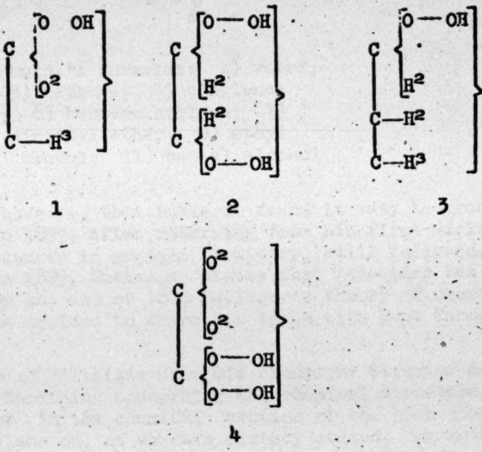


Fig. 3. Couper's formulas: 1) acetic acid; 2) ethylene glycol; 3) n-propyl alcohol; 4) oxalic acid.

In his article Couper gives also a number of incorrect formulas, e.g., those for oxalic acid, glycerol, and others. Couper's scientific activity was suddenly cut short, and he was not able to publish the second article that he had promised on the question of the structure of chemical compounds.

Somewhat later, an article by the German physicist Loschmidt appeared. In this, an enormous number of "constitutional formulas of organic chemistry in graphical representation", based on purely speculative considerations, were given. The spheres of action of the supposed atomic forces were represented by Loschmidt by circles of various diameters. As an example, I am giving a few of Loschmidt's formulas (Fig. 4).

Here I wish particularly to state and to emphasize that the purely speculative attempts of Couper and Loschmidt to represent the structures of organic compounds, attempts that were not based on experimental material and not supported by any factual results, passed at the time almost unnoticed and therefore did not and could not influence the course of the development of the problem of the structure of organic ~~or~~, in the widest sense, chemical compounds.

This, in a few coarse strokes, is my picture of the state of theoretical ideas in chemistry at the end of the sixties and beginning of the seventies of the last century. There was a feeling that a new phase in the evolution of chemistry was about to begin, but it needed the genius of Butlerov for the Rubicon to be crossed and for science to move forward.

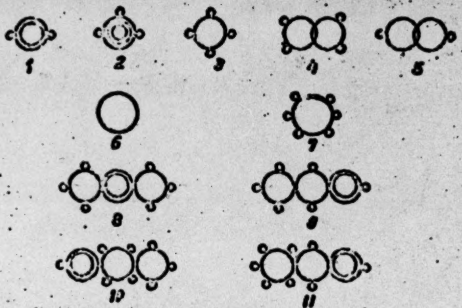


Fig. 4. Loschmidt's formules: 1) water; 2) ammonia; 3) methane; 4) ethylene; 5) acetylene; 6) benzene nucleus; 7) benzene; 8) dimethyl ether; 9) ethyl alcohol; 10) cresol; 11) benzyl alcohol.

It must not be thought, however, that Butlerov found it easy to cross the Rubicon, as I have put it. In 1857, after returning from his first visit abroad, Butlerov gave his students a course in organic chemistry, still following Gerhardt's system, but already in 1859, Butlerov states that "the time has come for us to go beyond Gerhardt". By the end of 1860 Butlerov's theory of chemical structure had fully matured, and he decided to share his ideas with West European chemists.

The paper under the title of ''Einiges uber die chemische Structur der Korper" - or translated literally: "Something concerning the chemical structure of bodies" - was read by Butlerov in the chemical section of the 36th congress of German naturalists and physicians on, as we have already stated, September 19th, 1861 at Speyer. This paper is remarkable in that Butlerov, for the first time in the history of chemistry, clearly states the questions at issue concerning the current situation in theoretical chemistry and announces the basic theses of the theory of the structure of organic compounds.

The Russian text of Butlerov's paper, with certain editorial changes, was printed in 1862 in the Scientific Memoirs of Kazan University under the title: "Concerning the chemical structure of substances", it formed an appendix to Butlerov's account of his visit abroad.

Permit me now to dwell on some of the more important points in Butlerov's paper. These consist above all in the definition of the concept of "chemical structure", which Butlerov, in his paper, formulates as follows: "Starting from the idea that every chemical atom that enters into the composition of a body takes part in the formation of the latter and acts there with a definite amount of the chemical force (affinity) that is inherent in it, I give the name of chemical structure to the disposition of these forces, in consequence of which the chemical atoms, acting directly or indirectly upon one another, unite together to form a chemical particle"'. This definition of Butlerov is so wide that it does not depart in essence from that which we understand by chemical affinity at the present time, in the light of modern ideas concerning the structure of the atom and of the molecule.

The greatest importance must be attached also to the part of the paper in which Butlerov speaks of the possibility of arriving at the structure of the particles of a substance by chemical methods, particularly by the methods of synthesis of organic compounds.

On this subject Butlerov states in his paper: "Conclusions concerning the chemical structure of substances probably can be based most satisfactorily on a study of the methods of their synthesis, preferably on such syntheses that can be carried out at temperatures not greatly above normal and, in general, under conditions that allow the gradual building up of the complex chemical particle to be followed".

Later in his paper, Butlerov gives 8 rules for the determination of chemical structure. "In the present state of our knowledge," states Butlerov, "the determination of chemical structure can be aided by the following rules, which are deduced from facts and are in part already accepted by the majority of chemists." I shall not go into details and cite these eight rules. However, the most important place in Butlerov's paper is that in which he considers the question of the possibility of expressing the structure of any substance by means of rational formulas.

As I have indicated briefly above, the term "rational formula" has been understood in different ways by various chemists at various stages of the evolution of chemistry. I will again mention that, e.g., Gerhardt and, later, Kekule and many other chemists considered it possible and, in fact, essential to express the structure of one and the same substance by means of several rational formulas. On this question of principle, Butlerov's stand was quite distinct from the views and convictions of all his predecessors. Butlerov, in fact, in contrast to Gerhardt, Kolbe, Kekule, and other chemists, considered it possible and essential to express the structure of a definite compound by means of a single rational formula, i.e., a single structural formula. In his paper, Butlerov defines the content of the term "rational formula" in this way: "If we now make an attempt to determine the chemical structure of substances, and if we succeed in expressing it in our formulas, then these formulas will be approximations, in known measure, to the true rational formulas. In this sense," says Butlerov, "only one rational formula is possible for each substance, and when the general laws relating the chemical properties of substances to their chemical structure become known, then such a formula will be an expression of all these properties."

This is the point in the paper that marks the Rubicon that Butlerov crossed, and it gives us the right to assert that Butlerov is the true creator of the theory of chemical structure. Extremely interesting and significant was the reaction of the majority of the chemists present at the congress to Butlerov's paper, in this, his first great appearance before a wide scientific audience. We may say, in short, that Butlerov's paper was coldly received by the audience. "Of all the chemists of that time," writes Markovnikov on this matter, "only the aged Heinz and the young privatdocent Erlenmeyer took up fully these new ideas and began to apply them in their articles; shortly afterwards, Wislicenus joined them." This state of affairs was very significant: it undoubtedly indicates the state of confusion that reigned in the minds of West European chemists concerning the most fundamental questions of theoretical chemistry.

On his return to Kazan from his visit abroad, Butlerov engaged in intense scientific activity, which was directed simultaneously in two directions - theoretical and experimental. First of all, Butlerov wrote a number of articles in Russian, German, and French, in which he developed his new theory of the structure of organic compounds in greater detail.

Butlerov, being dissatisfied with the development of the theoretical side, came to the conclusion that for the success and recognition of his new theory it was essential to obtain new facts in its support, and with exceptional energy he entered upon wide experimental investigations in the poorly equipped Kazan laboratory. The main result of this period was the celebrated Butlerov synthesis of trimethylcarbinol, the first representative of the class of tertiary alcohols, the existence and structure of which were predicted by Butlerov on the basis of his theory. The preparation by Butlerov of the first representative of an unknown class of tertiary alcohols was of great importance for the recognition and consolidation of the theory of chemical structure.

At this time, at the height of his creative powers, Butlerov prepared his famous textbook "Introduction to a Comprehensive Study of Organic Chemistry" for publication. The first Russian edition of this textbook appeared in 1864 and was completely sold out by 1866. Butlerov then made another very important step - he decided to publish his textbook in German. The German translation was published in Leipzig in 1868.

The publication in Russian and German by Butlerov of his textbook on the study of organic chemistry, a textbook in which, for the first time, the theory of structure was applied successively to all the classes of organic compounds, together with his brilliant researches, of which I have just spoken, changed the attitude of West European chemists to the theory of structure within a very short time.

Butlerov's theory of structure was not only accepted by the great majority of West European chemists, but what is more, Western science, particularly in the person of Kekule, started to dispute Butlerov's priority in the creation of the theory of chemical structure.

However, the little that I have been able to tell you concerning the evolution of the problem of the structure of matter shows without any doubt that not the insecure, inconsistent ideas of Kekule on this subject, nor the abstract notions of Couper and Loschmidt, but the strictly scientific and strictly logical conception of Butlerov was the turning point in the development of the science of chemistry, and I cannot refrain from repeating again that the inception of the new phase in the development of the theoretical basis of organic chemistry was made in Butlerov's paper of September 19, 1861.

It is very surprising that some scientists, only a few, it must be admitted, including even eminent scientists such as the French chemist Berthelot, did not recognize the theory of chemical structure for a long time. As is well known, Berthelot, during practically the whole of his long scientific career, did not acknowledge the reality of atoms, considered it even harmful for the development of chemistry to use the atomic theory, and used only equivalents in his numerous articles. This was Berthelot's position when Mendeleev discovered the periodic law and when, on the basis of this law, hitherto unknown elements were discovered.

It is not less surprising that the creator of the periodic law, Mendeleev, even after the discovery of the law, was critical in his attitude toward Butlerov's theory of structure and preferred to use his own modernized substitution theory in his organic chemistry course. A more stubborn and consistent opponent of the theory of chemical structure was the well known Russian organic chemist N. A. Menshutkin.

In a series of papers, e.g., in "Phenomena of Isomerism and their Explanation", Menshutkin defended views that were obviously out-of-date, and more than once Butlerov was forced to come forward, in his articles, in defense of his chemical structure theory. Of such articles, that entitled "The Theory of Structure and 'the Theory of Substitution'" was particularly remarkable for its strict exposition and its devastating criticism of Menshutkin's views. This article was published in 1885, a year before Butlerov's untimely death.

I will add that, when in 1898 I attended an organic chemistry course at Zaytsev, the textbook recommended to the students was the latest edition (1896) of Menshutkin's "Lectures on Organic Chemistry". In this edition, the lectures were based on Butlerov's theory of chemical structure, and in several places the significance of structural theory was emphasized. Thus, the last opponent of Butlerov's theory had been overcome.

I would like to conclude my paper by considering briefly what Butlerov's attitude was to the significance of theory and experiment in the realm of experimental sciences. Butlerov was of that rare type of scientist in which the genius of a theoretician is combined with a brilliant experimentalist, and therefore Butlerov's opinion on this matter is particularly valuable.

It seems to me that an almost exhaustive answer to this question was given in an obituary written by Butlerov on the occasion of the death of Academician Fritsche. This is what Butlerov wrote: "In chemistry we are accustomed to attribute the honor of discovery principally to the person who in fact made the discovery, and not to the one who predicted it on the basis of theory. Our theories are still far from perfection; they are born and they die, continually embracing a larger and larger circle of phenomena, but each theory in its time leads to the prediction of new facts – to discovery. To establish a theory – this is a great service; to predict a fact on the basis of the existing theory – this is within the reach of every chemist and may require but a few hours of time; but the factual proof or disproof of such a prediction may require whole months, sometimes years, of physical and mental effort."

A. E. Arbuzov

BLANK
PAGE

THE DEVELOPMENT OF ORGANIC CHEMISTRY IN THE LIGHT OF A. M. BUTLEROV'S TEACHING[1]

Ninety years ago, on September 19, (new style) 1861, at an international congress at Speyer, a young Russian chemist from distant Kazan read a paper on "The Chemical Structure of Substances", in which he expounded his views on the nature of organic compounds, a theory that he called "the theory of the structure of organic compounds". This paper heralded a whole era in the development of organic chemistry. The new approach, which will always be associated with the name of the great Russian chemist Butlerov, resulted in a remarkable development of organic chemistry and of the closely linked organic chemical industry during the whole of the succeeding period. For nearly a century it has been the lodestar that guides investigators on through the fantastic labyrinth of organic compounds. The orderliness of the grandiose system of organic compounds, built on the foundation of a few simple premises, namely, the valency of elements, the ability of carbon atoms to unite together in the form of long chains, and the disposition of atoms in space in accordance with the rules of valency, arouses involuntary surprise and amazement in all who make the acquaintance of organic chemistry.

Only 26 years before Butlerov's theory of structure came into being, Wohler wrote to Berzelius: "Just now, organic chemistry is enough to send a man out of his mind. It has the same effect on me as virgin tropical forest, full of remarkable things and of fantastic unending overgrowth from which it is impossible to extricate oneself and into which it is terrifying to plunge". How has it happened that this fantastic unending overgrowth of the virgin tropical forest of organic compounds has been converted into an orderly system in such a short time?

An enormous amount of experimental material accumulated by organic chemists has been clarified and put into strict order, thanks to the theory of structure. It is difficult to name any other theory that has shown the same ability to make predictions as Butlerov's theory of the structure of organic compounds. Tens and hundreds of thousands of compounds predicted by the theory of structure have been prepared and have served as a brilliant confirmation of the correctness of this theory. The whole of modern organic chemistry with its more than a million compounds is founded on Butlerov's theory of the structure of organic compounds. The work of Butlerov, the founder of the theory of the structure of organic compounds, raised Russian chemical science to an unprecedented level.

Very few scientific generalizations can be named that have turned out to be so fruitful as the theory of the structure of organic compounds. The basic premises of Butlerov's theory of the structure of organic compounds determined the path along which organic chemistry was to develop for a long way ahead. Butlerov's theory had a powerful fruitful influence also on inorganic and on physical chemistry. During the ninety years of its existence, from Butlerov up to our own day, the theory of structure has passed along its complicated evolutionary path. It often appeared that facts did not agree with the theory of structure, that they were in contradiction with it, but this non-accord always turned out to be only apparent and subsequently led only to reinforcement, deepening, and widening of the theory of structure. At first, the theory of structure represented the structure of organic compounds by plane formulas. However, in 1863, i.e., 11 years before the announcements of van't Hoff and le Bel, Butlerov wrote: "If atoms really exist, then I do not see why all our attempts to determine their disposition in space should be in vain, as Kolbe declares it is, and why the future should not be able to teach us how to carry out the required determinations." Thus, Butlerov foresaw the coming of stereochemistry.

---

[1] Paper read at a general meeting of the Division of Chemical Sciences held on September 26, 1951 in celebration of the completion of 90 years since A. M. Butlerov's paper on "The Chemical Structure of Substances."

Two decades had not passed since the coming of the theory of structure when the theory of the spatial disposition of atoms in the molecule appeared. It came into being as a result of the apparent non-correspondence between the number of isomers predicted on the basis of the premises of the classical theory of structure and the number of isomers actually found. Stereochemistry appeared as an inevitable consequence and development of Butlerov's theory of structure, and it gave invaluable results as regards our knowledge of organic substances, and later also of inorganic compounds. The theory of the asymmetric atom as the source of the optical activity of certain organic substances and the theory of the stereochemistry of unsaturated and cyclic compounds extended our ideas concerning the structure of organic compounds in an extraordinary fashion.

The discovery of optical activity in compounds that do not contain asymmetric atoms, as found in inositol and certain derivatives of biphenyl, gave new material for the study of the geometry of molecules. The theory of the spatial arrangement of atoms in the molecule not only led to the establishment of various types of stereoisomerism, but was extended also to the question of the effect of structure on the reactivity of organic compounds, one of the cardinal questions of organic chemistry, bringing in the concept of steric hindrance in chemical reactions.

The examination of the properties of cyclic compounds from the point of view of a few simplified geometrical concepts, led to the strain theory, which explains to a certain extent the variation in the properties of these organic substances according to the number of members of the ring. However, also in this case the properties of a number of cyclic compounds were not in complete agreement with the theory, e.g. in the case of five- and six-membered rings, and particularly in the case of many-membered rings containing 15-20 atoms in the ring. The discovery of the existence of many-membered rings and of their remarkable stability confirmed the necessity for regarding the disposition of the atoms in the ring not as being in a plane, but in space. All these results show that Butlerov's structural formulas are not the dry immutable schemes that they may appear to be at first glance.

Structural formulas reflect not the statics, but the dynamics of molecules. This is just how Butlerov regarded molecules. "At the present time," writes Butlerov, "we look upon a chemical compound not as something that is dead and stationary, but we assume, on the contrary, that it is endowed with constant movement, which is present in its very smallest particles, the individual mutual relations of which are undergoing constant changes, which all sum up together, however, as a sort of constant average result." Taking the formation of many-membered rings as our example, it can be shown how an examination of the spatial disposition of the atoms within the molecule, in their constant state of movement, enables us not only to explain the properties of the molecules, but also to predict the conditions that will be particularly favorable for the formation of such molecules, which are generally prepared with great difficulty.

I should like to point out the principle of high dilution in the synthesis of many-membered rings. The formation of a many-membered ring from molecules that are long and threadlike and have two functional groups at the ends of the chain is not very probable because there is a low probability of the ends of the chain coming sufficiently close together in the course of the movements of the threadlike molecule for the closure of the ring to become possible. The meeting of the functional groups of different molecules, which would lead to the formation of linear polymers, is much more probable. By diluting the initial bifunctional compound with an inert solvent, it is possible to reduce the probability of encounters between functional groups of different molecules and increase the probability of an approach to within a short distance of the functional groups of one and the same molecule, thus increasing the probability of the closing of the many-membered ring. By applying this principle of high dilution; taking, for example, 1.5 g of initial substance and diluting with 9 liters of solvent, it is possible to obtain high yields of the many-membered ring.

I think that these examples show quite clearly that Butlerov's theory of the structure of organic compounds, enriched by spatial concepts, correctly portrays the kinetic condition of the molecules. The extension of inferences from the theory of structure and from stereochemical concepts to inorganic compounds has undoubtedly had a great influence on the emergence and development of coordination theory. At the basis of Butlerov's teaching lies the concept of the linkage of atoms in the molecule in accordance with valency rules.

For carbon, the essential element of organic substances, chemists came to recognize, after some vacillation, a constant valency of four. The exception was carbon monoxide. However, it was later necessary to acknowledge the presence of bivalent carbon in whole classes of organic compounds: the isonitriles and derivatives of fulminic acid. In 1900, the possibility of the existence of tervalent carbon was discovered for the first time, the example being triphenylmethyl; later the existence in other elements of abnormal valency was discovered. Free radicals containing tervalent carbon and bi- and quadri-valent nitrogen were prepared only in the case of heavy aromatic radicals.

All attempts at preparing free radicals of the aliphatic series were invariably unsuccessful, but in 1929 the free radical methyl was prepared and the possibility of the existence of simple aliphatic radicals was thus demonstrated. Also, the reason for previous lack of success became understandable. The life of the free methyl radical turned out to be very short, the half-life being only 0.006 sec. Organic chemistry was enriched by an interesting peculiar group of compounds. At first it seemed that this group of organic compounds would be very much circumscribed with respect to the conditions of their formation and existence. However, the further development of this branch of organic chemistry has shown the reverse.

It has been found that the simple free radicals derived from tervalent carbon are formed in a number of processes that are important both from the theoretical and the practical points of view, and that they play an essential role in these reactions. Free radicals play an important part in the pyrogenetic decomposition of organic substances in the cracking process. A prominent role is to be attributed to free radicals in various polymerization processes that yield products of great practical importance. Free radicals play an essential part in photochemical processes, the reactions of diazo compounds, catalytic halogenation, and many other processes. Free radicals, the existence of which seemed to be so improbable when triphenylmethyl was discovered, since they did not conform to the concepts of the theory of structure, later resulted in development and enrichment of this theory.

In considering the development of organic chemistry during the time from the inception of the theory up to the present time, it is impossible not to take note of the progress that has been made in these 90 years in the study of macromolecular compounds, both natural and synthetic. The chemistry of macromolecular compounds began to develop considerably later, which is quite understandable if the difficulties that are met in their study are taken into consideration. Macromolecular compounds were at first regarded as being made up of small highly associated cells, and colloidal solutions of macromolecular compounds as consisting of colloidal particles of micellar structure. It therefore appeared that the theory of structure of organic compounds did not have the same significance in this sphere as it has for low-molecular-weight compounds. It appeared that for the majority of macromolecular compounds the question of the elucidation of their structure and the structure of their colloidal solutions was a problem rather for colloid chemistry than for organic chemistry. Nevertheless, this turned out to be incorrect, and for the majority of typical macromolecular compounds, both natural and synthetic, the application of the theory of structure has been found to be correct and fruitful.

It is now quite obvious that the gigantic molecules of macromolecular compounds are true molecules. Thousands of carbon atoms may be united one to another forming long threadlike molecules or fantastic three-dimensional network structures. Organic chemistry has been enriched by a new sphere of colossal theoretical and practical significance – the chemistry of macromolecular compounds, while the theory of structure has been enriched by new ideas and concepts, such as the concept of polymer-homologous series, etc.

In considering the development of organic chemistry it is impossible not to take note, even if only very briefly, of the achievements in the study of natural substances that play an enormous part in the life processes of animal and vegetable organisms. While at the end of the last century and the beginning of the present century fundamental investigations were made into the nature of compounds found in nature in large amounts, the last 20-30 years has been characterized by great success in the study of compounds that are formed in living organisms in negligible amount and yet play an important part in their life processes. I am thinking of the progress made in our knowledge of the nature of vitamins, hormones, and antibiotics.

The characteristic peculiarity of these investigations has been processes in which we pass from hugh quantities of initial materials, often expressed in thousands of kilograms, on to insignificant amounts of end products, expressed in grams, or sometimes in tenths, hundredths, or even thousandths of a gram. Thanks to the development of micro-analysis and of methods of dealing with very small amounts of material, it became possible to establish the structures of complex substances, in spite of the fact that they were available in quantities that would at one time not have sufficed for a single elementary analysis.

It should be noted that, while on the one hand organic chemistry has given medicine a powerful weapon in its fight against disease, in the form of various medicinal preparations, and has helped to some extent to elucidate the nature of the processes that accompany various departures from normal functioning in an organism, on the other hand the demands of practice have stimulated investigations in particular branches of organic chemistry, leading to their rapid development. Thus we have the example of the influence exerted by the problem of experimental cancer on the development of the chemistry of polynuclear compounds of aromatic character; also, the influence of the study of the nature of the sex hormones on the chemistry of the hydrogenated derivatives of phenanthrene and related substances.

Study of the nature of vitamins and the problem of their synthesis led to intensified development in certain sections of the chemistry of heterocyclic compounds. Sometimes, as in the case of sulfamide preparations, many thousands of new compounds were synthesized with the result that perhaps ten might be applied widely in medical practice. All this progress in organic chemistry became possible only on the basis of Butlerov's theory of structure.

Placed at the basis of Butlerov's theory of the structure of organic compounds is the idea that "the chemical nature of a complex molecule is determined by the nature and number of its elementary component parts and by its chemical structure". Chemical structure is often erroneously regarded as merely the relative disposition of the atoms in the molecule, which are united together in accordance with the rules of valency. Butlerov's views on the structure of an organic molecule were wider and deeper than this.

Already in his paper at the international congress at Speyer in 1861 Butlerov states that atoms, by directly or indirectly acting upon one another, are linked together to form the chemical particle - the molecule. This idea of the mutual interaction of atoms in a molecule, whether they be directly united one to another or not, was frequently expressed by Butlerov. This idea of Butlerov was more fully developed later by his eminent pupil and follower Markovnikov. In his famous dissertation, "The Mutual Effects of Atoms in Chemical Compounds" (1869), Markovnikov wrote: "The question of the effect of elementary atoms on the course of the chemical reactions of a complex body is one of the most thrilling questions of modern chemistry and, as is already noticeable, is occupying more and more of the attention of chemists". This question of the interaction of atoms in the molecule of an organic substance and of the effect of the structure on the reactivity of the molecule is still one of the most thrilling and vital questions of present-day organic chemistry.

Neither Butlerov nor Markovnikov were in a position to explain the mechanism of the transmission of mutual effects of atoms in the molecule. They could not explain what was hidden behind the line that was used to indicate the linking together of atoms in the molecule. Naturally, the state of knowledge at that time was such that it would have been difficult to demand an answer to this sort of question from the theory of structure.

Also, the separate chemical bonds in the structural formulas were not all identical to the organic chemist, in spite of being denoted in all cases by the same sign - a line.

The formal language of structural theory - a line to indicate a single bond between atoms, or lines to indicate double or triple bonds - is too meager for the expression of all the variety in chemical behavior of the various atoms and groups of atoms in the molecule of an organic substance. This diversity in chemical behavior of atoms or groups of atoms is associated by the organic chemist with the general structure of the molecule and is an expression of the rich experimental material accumulated by organic chemistry, and it certainly cannot be directly represented by a line, as such.

Organic chemists have long felt the inadequacy of the language of classical structural theory, and this has led to the emergence of supplementary hypotheses of oscillating valencies, partial valencies, etc. Nevertheless, these supplementary hypotheses also were unable to explain satisfactorily the experimental results that were being yielded by the rapidly expanding organic chemistry. By way of example, we may point to the disillusionment of Thiele regarding his theory of partial valencies and to the pessimistic conclusions of Wislicenus, when he surveyed his life-work on tautomerism. This rich experimental material has been brought together by organic chemists in the form of so-called rules. In this way there arose the rules of Markovnikov, Eltekov, Zaytsev, Popov, etc.

However, in spite of the imperfections of the language of structural theory, organic chemists, by applying this theory, succeeded in correctly establishing the structures of extremely complex organic compounds. They succeeded in establishing the structure correctly even when the reactions used as a means of establishing the structure went in an abnormal fashion and were accompanied by a rearrangement, sometimes a far-reaching rearrangement of the skeleton of the molecule, i.e. the type of reaction that is accompanied by all sorts of isomerizations and regroupings. Among the investigations of this sort are the classical researches of Butlerov's pupil Vagner in the terpene field, the work of Demyanov on the isomerization of rings, and many others. These instances, which at first glance did not seem to agree with inferences from the theory of structure, later served only to strengthen and extend it.

Since the time of Butlerov's paper at Speyer, 90 years have passed. During this period there have been some very great discoveries contributing to our knowledge of matter. The atom has turned out to be a complex system. Our concept of the nature of the chemical bond has been changed and deepened. Our ideas concerning the structure of organic molecules and of the mechanism of chemical processes have been extended and enriched. All this progress and these new ideas were bound to be reflected in the theory of the structure of organic compounds. The development of our knowledge concerning the structure of the atom made it necessary to link these ideas with the classical theory of structure, and this was done. Gradually electronic concepts penetrated more and more into organic chemistry. At first, the electronic formulas were merely restatements of the classical structural formulas in electronic language. Later, electronic ideas were able to explain the non-equivalence of the various covalent bonds, which is the result of mutual effects of atoms or groups within the molecule. The basis of these ideas was the concept of electronic displacements, brought about by internal and external causes. The concept of electronic displacements, characteristic of the state of polarization or the polarizability of the molecules, i.e. the distribution of electron density in the molecule, enabled a clearer picture to be formed of the mutual effects of atoms in molecules and of the transmission of these effects. To a certain extent it gave an explanation for the peculiarities in behavior of conjugated systems of double bonds and of aromatic and other compounds, and it led to the discovery of the phenomenon of vinylogy.

Concepts concerning the variation in electron density in various parts of a molecule, due to internal or external causes, enabled a clear picture to be formed of the basis of the rules of Markovnikov and Eltekov concerning the orienting effects of substituents in the benzene nucleus. On the basis of ideas concerning the electron density in a molecule, concepts were worked out relating to the electron-donating (nucleophilic) and electron-accepting (electrophilic) characters of reagents. These concepts constitute a step forward in the development of Butlerov's theory of structure, in the theory of the mutual effects of atoms in a molecule, and in the theory of the relation between molecular structure and reactivity. These concepts, however, are far from perfect. They permit only a qualitative explanation of the mutual effects of atoms linked together in a molecule. The method of representing electron density distribution is imperfect. It has many deficiencies, the main one being that, with this method of representation, the state of a molecule of an organic compound can be interpreted both from the point of view of the materialistic theory of Butlerov and also in the spirit of the idealistic teaching of the so-called "theory of resonance".

At first the concept of electron displacements was directed towards the interpretation of experimental data concerning the effects of atoms or groups of atoms forming part of the molecule on the behavior of the molecule as a whole. Later, however, the most prominent representative of this school, the English chemist Ingold, went over to the erroneous idealistic concept of electronic resonance.

A fundamental part in the development of our concepts concerning the nature of chemical affinity and of the structure of organic molecules has been played by the application to chemistry of quantum mechanics. Quantum chemistry has enabled new concepts concerning the nature of the chemical bond to be formed.

The application of quantum mechanics to questions in the theory of structure has enabled a physical basis to be given to some of the fundamental premises of this theory. Quantum chemistry has given an explanation of the nature of the capacity for saturation in a chemical bond, of the tetrahedral configuration of the carbon atom in saturated compounds, and of the characteristics of multiple bonds. Certain predictions of quantum chemistry have received experimental confirmation, as, for example, the effect of co-planarity on the properties of molecules containing conjugated bonds.

The field of applicability of quantum-mechanical calculations, however, is limited to only the very simplest molecules; quantum-mechanical calculations on polyatomic molecules are extremely approximate, and quantitative results obtained by their aid are not reliable. Hence, these calculations permit only general qualitative inferences that may permit some of the peculiarities of complex molecules to be interpreted. The progress that I have indicated in the development of our concepts concerning the nature of organic molecules and the course of the chemical changes of these molecules is based on the further development and deepening of Butlerov's teaching.

In the last 10-15 years, attempts have been made to revise the principles of Butlerov's theory of structure, as if it were not able to explain the properties of organic compounds and, to represent correctly the nature of the processes determing the course of chemical reactions. These attempts come from the adherents of the "theory of resonance", which is bound, in the opinion of those adherents, to replace Butlerov's theory of structure. This "theory" lays claim to a leading role in organic, physical, and inorganic chemistry, to the role of a universal theory that has its source directly in the concepts of contemporary quantum mechanics. This theory has received wide acceptance among foreign chemists and also within a certain section of Soviet chemists.

During the last 2-3 years, the "theory of resonance" has been subjected to detailed analysis and justifiable criticism in a series of discussions and conferences, and in our journals. These discussions have made abundantly clear the erroneous and idealistic nature of this "theory" and the harm that it has done to the development of the theory of chemical structure, diverting workers from the true path and creating the harmful illusion of explaining observed facts, which, in fact, remain unexplained.

In describing the development of the theory of the structure of organic compounds, I consider it essential to point out the part played by physical and physico-chemical methods in the study of the structure of organic compounds. Physical methods of investigating the structure of organic compounds have given and are still giving invaluable help in the task of determining the nature of organic substances. Spectroscopic, electronographic, and X-ray analysis methods, and also the method of dipole moment determination, have enabled all the fundamental parameters of organic molecules to be determined. They have permitted us to determine the configurations of the atoms linked together in the molecule, to estimate the valency angles, to determine the interatomic distances within hundredths of an Angstrom, and to find the distribution of electron density in various parts of the molecule. Magnetic methods of investigation are the best for the detection of free radicals.

Physical methods are of very great importance in the study of macromolecular compounds and of catalytic and many other processes. Physical methods of investigating the structure of organic compounds have confirmed the postulates on which the theory of structure is based and have furnished weighty evidence for the correctness of the theory. The structure of the molecules of organic compounds - the concept that lies at the basis of Butlerov's ideas - is an actual reality. We are not only certain that the atoms are united one to another in accordance with the laws of valency, as follows from Butlerov's theory of structure, but we can measure the distances between these atoms to an accuracy of a few millionths of a millimeter.

By the aid of a beam of electrons we may almost photograph the molecules of organic compounds. The pictures obtained of the structures of the most complex organic molecules, such, for example, as the phthalocyanines, by analysis of their electronograms coincide exactly with the structural formulas derived on the basis of Butlerov's classical theory of structure. By way of example we will consider platinum phthalocyanine.

On Figure 1 is shown the structural formula of platinum phthalocyanine constructed in accordance with Butlerov's theory. On Figure 2 is shown the electronogram of the same compound.

In order to make the striking correspondence between the structural formula of platinum phthalocyanine and its electronogram still clearer, the structural formula of the phthalocyanine has been superimposed on the electronogram in Figure 3.

Ninety years have passed since the theory of structure was created, and it still remains the basis of modern organic chemistry and for yet a long time to come will remain the foundation of our knowledge of organic substances. For almost a century the theory of structure has been the guiding thread for organic chemistry. Few scientific generalizations could be named that have stood firm for so long a time.

What then is the reason for the great importance of the theory of structure?

It is that at the basis of the immense importance of Butlerov's theory of structure and of its immutable nature lies a true portrayal in its materialistic character of the actual real world. The correctness of the theory of structure has been verified countless times and is being verified in practice at present. This verification has been done and is being done both in laboratories and also in industry, in the manufacture of organic substances on an immense scale in the factories. Right up to the present time, Butlerov's theory of structure continues to give organic chemistry a powerful stimulus to further development.

Nevertheless, however great may be the progress of organic chemistry, and however great may be the importance of the theory of structure, we must still remember the remarkable words of its founder Butlerov when, in considering the

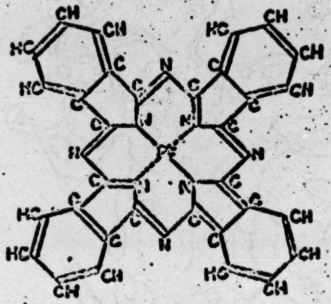

CH
CH
HC
HC
C
C
N
C
C
HC
CH
CH
C
C
CH
N
N
C
C
N
N
C
N
C
N
C
C
C
HC
CH
HC
C
C
N
C
C
HC
CH
CH
CH
HC
CH

Fig. 1

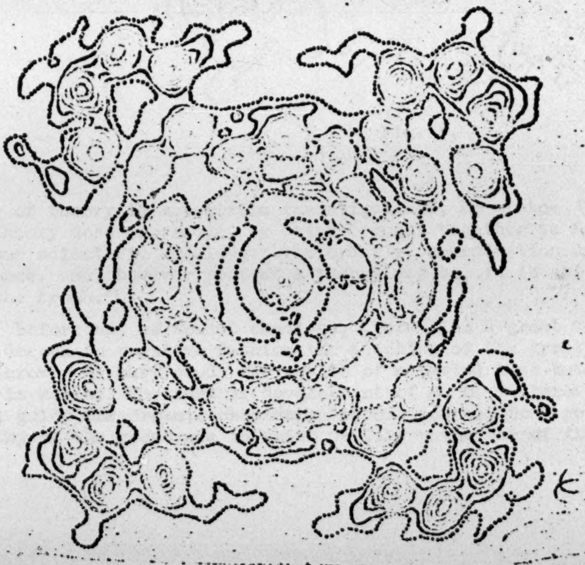


Fig. 2

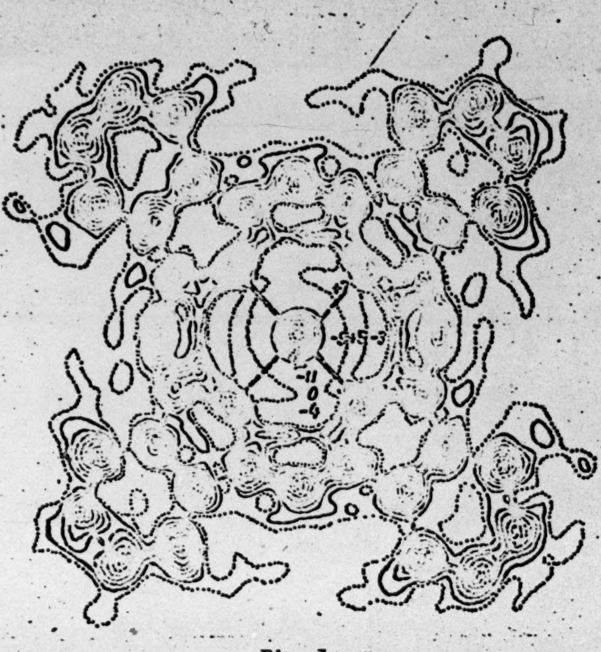


Fig. 3.

role of theory in scientific investigations, he wrote: "Only through the medium of theory does knowledge, by being brought together to form a connected whole, become scientific knowledge; the orderly coordination of knowledge constitutes science. But however perfect a theory may be, it is still only an approximation to the truth."

Before us, as Soviet chemists, there lies a great and noble task: to extend and deepen in creative fashion the teaching of the great Russian chemist Butlerov. We must study the wealth of material that Butlerov has left to us in his works. The further development of A. M. Butlerov's theory of structure will guide the organic chemistry of our country to a yet fuller blossoming worthy of the great era in which we live – the era of the building of communism.

B. A. Arbuzov

PHENOL COMPOUNDS OF THE INERT GASES AND THEIR ANALOGS

B. A. Nikitin and M. P. Kovalskaya

In previous investigations it has been shown that the inert gases, as well as giving the already known hydrates, give also compounds with phenol and toluene [1]. At the same time it was established that in their formation of molecular compounds the inert gases have numerous analogs among the volatile hydrides and also, in the case of the hydrates, among substances whose molecules contain many atoms. This analogy is shown above all in the similarity of the conditions of formation and, particularly, in their isomorphism. Foreign workers [2] have established the formula $H_2S \cdot 2C_6H_5OH$ for the compound of hydrogen sulfide and phenol, using fusion diagrams. Nikitin [3] showed that the inert gases are isomorphously co-precipitated with the H_2S – phenol compound, and he concluded that the inert gases form analogous compounds, to which he ascribed the same type of formula. Later, he prepared directly compounds of xenon and krypton with phenol [4], but the thermal analysis of the H_2S – phenol system was done only from the liquidus curve and without taking into account the amount of hydrogen sulfide remaining in the gas phase. By the use of a specially developed method for the thermal analysis of systems containing a volatile component, Nikitin, Kovalskaya, and Pushlenkov [5] carried out a more accurate determination of the fusion diagram for this system and showed that the compound must be assigned the formula $H_2S \cdot 3C_6H_5OH$.

A question of great interest for the further development of the chemistry of the inert gases is the determination of what substances behave in analogous fashion with respect to the formation of compounds with phenol. As the hydrates of the inert gases not only have an analogous formula to the hexahydrate of SO_2, but are also isomorphous with it [6], we decided to examine whether this analogy is shown also in the compounds with phenol, using radon as our example. If radon is taken up from the gas phase by crystals of the SO_2 – phenol compound and this capture proceeds according to Khlopin's isomorphous co-precipitation law, then both the isomorphism and the analogy in formula will be shown for these compounds [1]. The investigational method was the same as that used in the study of the co-precipitation of radon with crystals of the H_2S – phenol compound [3]. Finely ground, carefully dried phenol was introduced into a U-tube having a ground joint and two taps. The volume of the gas phase was then measured, and a definite amount of SO_2 was introduced into the reaction tube. A compound was formed from the gaseous SO_2 and the solid phenol, the temperature being below that of the eutectic. In one series of experiments, some radon was first admixed with the sulfur dioxide, and under these conditions the crystals of the compound took up radon at the moment of their formation. The tube was then allowed to stand for a long time to permit the attainment of equilibrium in the distribution of radon between the gas phase and the crystals of the compound (Method I).

In another series of experiments, the compound was formed in absence of radon, which was then introduced into the reaction tube. By carrying out the complete recrystallization of the compound, uptake of radon was promoted and a state of equilibrium in its distribution between the gas phase and the crystals of the SO_2 compound was attained (Method II). The amount of radon taken in each experiment was about 10^{-12} g. Knowing the dissociation pressure of the SO_2 compound, the volume of the gas phase, and the amount of SO_2 taken for the experiment, it is easy to calculate the amount of SO_2 in the gas and in the solid phase. At the end of the experiment, the tube was cleared by means of a stream of air containing sulfur dioxide in such amount that its partial pressure corresponded to the dissociation pressure of the compound at the given temperature. This prevented decomposition of the compound during the clearing. The radon was determined radiometrically both in the gas phase and in the air-swept crystals. If repeated recrystallization of the compounds of SO_2 (the macro-component) has resulted in the establishment of equilibrium in the distribution of radon (the micro-component) between the gas and solid phases, then the distribution must be in accord with Khlopin's law:

$$\frac{\%\text{Rn in cryst. phase}}{\%\text{Rn in gas phase}} = D\,\frac{\%SO_2\text{ in cryst.phase}}{\%SO_2\text{ in gas phase}}$$

where D is a constant at a given temperature. The experiments were carried out at 0°. The results are given in Table 1.

TABLE 1

Method	Duration of recrystallization in hours	% SO_2 in crystals	% Rn in crystals	D
I	72	77.2	45.4	0.25
II	120	80.0	54.7	0.30
I	67	89.8	75.7	0.35
II	120	90.3	71.0	0.26
I	24	96.5	88.9	0.30
II	73	97.1	92.1	0.35
I	24	97.6	92.9	0.32
II	74	98.0	93.9	0.31
			Mean	0.30±0.03

From this table it will be seen that radon is readily taken up by crystals of the compound of SO_2 with phenol and that the capture proceeds according to the amorphous co-precipitation law, for the distribution constant D remains, in fact, constant within limits of experimental error (about ± 10%); at 15°, D = 0.24.

According to the isomorphous co-precipitation law, the compound of Rn with phenol should have a formula that is analogous to that of the SO_2 – phenol compound. For the compound of H_2S with phenol we have already established the formula $H_2S\cdot3C_6H_5OH$ and have shown that radon is isomorphously co-precipitated with it (at +15°, D = 1.25). However, the compound of SO_2 with phenol has hitherto been assigned another formula. It was first prepared by Meyer and Kolbe (8) already in 1881. On the basis of the results of the analysis of the compound they assigned it the formula: $SO_2\cdot4C_6H_5OH$ or $SO_2\cdot5C_6H_5OH$. Since the compound dissociates appreciably in the air with loss of sulfur dioxide and the authors took no precautions during the analysis, their proposed formulas do not appear very convincing.

We decided to determine the formula of this compound by means of thermal analysis, using the procedure we had worked out earlier for analogous systems [5]. As the system contains a volatile component, it was necessary first to determine the temperature – pressure diagram when the system contains three phases – solid, liquid, and gas – in equilibrium. This is required to enable a correction to be made for the amount of sulfur dioxide remaining in the gas phase when calculating the molecular ratio of components in the course of constructing the fusion diagram.

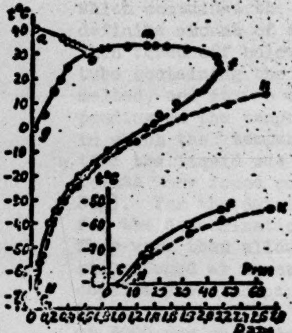


Fig. 1. Temperature - pressure diagram for the system SO_2 - C_6H_5OH

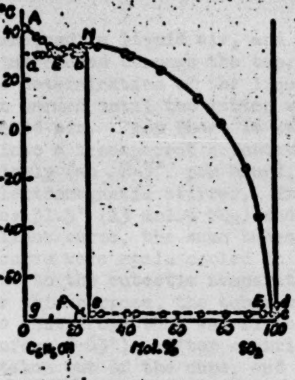


Fig. 2. Fusion diagram for the system SO_2 - C_6H_5OH

The phenol used in these investigations melted at 41.0° and boiled at 180°. According to analysis, the sulfur dioxide contained less than 0.5% impurity. A weighed amount of carefully dried phenol was introduced into a glass tube made from barometer tubing and having a capacity of 2-3 ml. The tube was fused to a glass mercury manometer graduated up to 10 atm. The air was then pumped out of the apparatus, the tube was cooled in liquid air, and from an attached buret a definite amount of sulfur dioxide was introduced. The tube through which the sulfur dioxide was introduced was then sealed off so that the apparatus was now hermetically sealed. In the tube containing the substance there was a small electromagnetic stirrer, which was placed there beforehand.

In order to determine the equilibrium pressure, the tube containing the substance was maintained at a definite temperature in a cryostat or thermostat, and the liquid was vigorously stirred with the electromagnetic stirrer. The results obtained are shown graphically in Fig. 1. The curve ae on this diagram shows the dependence of pressure on temperature when gaseous SO_2, the melt, and solid phenol are in equilibrium. Point e corresponds to the eutectic point. The curve emfN relates to the case where the solid phase is a compound. It is already evident from this diagram that a compound is formed in the system with a melting point of 34.2°. For comparison, the curve NK has been inserted in the diagram; it shows the variation of the vapor pressure of pure SO_2 with temperature. Curve ge shows the dissociation pressure for the conversion of the solid compound into solid phenol and gaseous sulfur dioxide.

It was found impossible to determine the fusion diagram by the method of temperature halts because a great deal of supercooling is observed in the SO_2 - phenol system. Hence, we determined the liquidus curve visually by noting the temperature at which the last crystal disappeared, the liquid being constantly stirred. We determined the solidus curve by centrifuging sealed tubes at temperatures as close as possible to the eutectic temperature, following the method already developed. A piece of barometer tubing blown out at the fused end served as reaction vessel. At the other end of the tube there was a ground joint, and through this joint a definite weight of phenol was introduced, and the electromagnetic stirrer was inserted. A glass vacuum tap was then inserted into the joint, and the air was pumped out of the tube. The blown-out end of the tube, which contained the phenol, was then immersed in liquid air, and from a buret a definite amount of sulfur dioxide was introduced through the tap. The tube was then fused off below the joint. In the determination of the liquidus curve, the tube containing the substance was first warmed until the latter was completely melted, and it was then immersed in liquid air. From there it was removed, depending on the temperature of fusion, into a transparent cryostat or thermostat, in which the temperature was raised slowly (at 2-3° per hour). At the same time the liquid was stirred with the electromagnetic stirrer. Two eutectic points were found on the liquidus curve: 31.5° (13 mol.% SO_2) and −75° (98.8 mol.% SO_2). For the determination of the solidus curve, the same tubes that were used for the determination of the liquidus curve were again cooled in liquid air. They were then allowed to stand at close to the eutectic temperatures and were centrifuged at these temperatures. For this purpose, the tubes were immersed, capillary end downwards, in a cup of the centrifuge that was filled with crystallizing guaiacol (29°) or melting chloroform (−63°). After centrifuging for 3 min. at 3000 rev. per min., the tubes were taken out of the cups, and the presence or absence of liquid in the capillary was determined visually. The tube was then opened and its capacity determined. The volumes of the stirrer and of the liquid and solid phases were subtracted from the value obtained, thus giving the volume of the gas phase. The amount of sulfur dioxide remaining in the gas phase was calculated from the pressure − temperature diagram, and this was subtracted from the amount of SO_2 taken for the experiment. As the maximum pressure in the system did not exceed 2.2 atm. and the dead space was not more than 1 ml, the correction was not greater than 2.5%. 0.5-0.01 g phenol and 5-200 ml SO_2 were taken for the experiment.

It must be noted that, owing to the variation of the pressure of SO_2 with temperature, for a given tube the points on the liquidus and on the solidus curve corresponded to different molecular percentages of SO_2. The results obtained are shown in Table 2 and on Fig. 2. At 29°, samples No. 2 − 8 showed no trace of liquid. On allowing them to stand in a thermostat (at 32°) with their capillary ends downwards, liquid could be seen running down the capillary. This crystallized with supercooling, but in all cases the crystals formed largely melted at 31.5°, since they consisted of almost pure eutectic mixture. In sample No. 9, liquid could be observed at 33.5°.

On centrifuging tubes No. 10 − 20 in melting chloroform (−63°), liquid appeared in the capillary in all cases. After the complete crystallization of this liquid at lower temperatures, the commencement of fusion of the crystals formed was observed in all cases at −75°. It follows from all these results that the line denoting the composition of the compound must be drawn at 25 mol.% SO_2, and that the compound must be assigned the formula $SO_2 \cdot 3C_6H_5OH$.

As the pressures in the system SO_2 − phenol turned out to be low, we decided to make an attempt to analyze the compound also chemically. For this purpose, a weighed amount of phenol was introduced into a U-tube having a joint and two taps. The air was then pumped out of the tube, and sulfur dioxide was introduced into the tube at −15° in amount sufficient to dissolve the phenol completely. The tube was then cooled until crystals of the compound made their appearance. The greater part of the sulfur dioxide was then removed by pumping. A manometer was attached, and pumping was continued at 0° until the pressure fell to 72 mm (the dissociation pressure of the compound [giving solid phenol and gaseous SO_2] at 0°). The crystals should now constitute a pure compound. The amount of SO_2 remaining in the gas phase was taken into account. NaOH solution was then introduced into the tube, so that the compound was completely decomposed. This procedure fully ensured that SO_2 would not be lost, but it did not preclude the possibility that

TABLE 2

No. of tube	Mol.% SO_2	Temperature at end of fusion (°C)	No. of tube	Mol.% SO_2	Temperature at beginning of fusion (°C)
1	0.00	41.0			
2	4.74	37.6	2	4.59	31.5
3	6.88	36.4	3	6.81	31.5
4	9.73	33.9	4	9.73	31.5
5	10.02	32.4	5	10.02	31.5
6	14.79	32.6	6	14.89	31.5
7	19.52	33.8	7	19.63	31.5
8	22.79	34.2	8	22.90	31.5
9	24.85	34.2	9	24.85	33.5
10	26.34	34.1	10	26.98	-75.0
11	29.49	33.9	11	29.80	-75.0
12	40.73	31.4	12	41.28	-75.0
13	42.91	30.0	13	43.43	-75.0
14	54.24	24.4	14	54.68	-75.0
15	69.74	13.2	15	69.98	-75.0
16	79.42	3.4	16	79.51	-75.0
17	89.50	-15.0	17	89.61	-75.0
18	95.02	-35.0	18	95.02	-75.0
19	98.79	-75.0	19	98.79	-75.0
20	98.94	-74.0	20	98.94	-75.0
21	100.00	-73.0	21	100.0	-73.0

mother liquor would be retained by the crystals and might therefore give high values for the amount of SO_2. The sulfur dioxide was oxidized with hydrogen peroxide, and the sulfate ions formed were precipitated with barium chloride. The following results were obtained in this way:

To each mol. SO_2 – 2.86; 2.79; 2.90; 2.86 mol. C_6H_5OH.
Mean: 2.87 mol. C_6H_5OH per mol. SO_2

Hence, the results of thermal and of chemical analysis are in good agreement. This shows that the compound has the formula $SO_2 \cdot 3C_6H_5OH$, analogous to the formula of the compound of H_2S with phenol.

Nikitin [4] has previously prepared a compound of HCl with phenol and has shown its isomorphism with the xenon-phenol compound by tensimetric analysis. We decided to try to determine the formula of the compound of HCl with phenol. This compound melts congruently at 35.9°. The part of the fusion diagram that we have determined in the region close to the composition of the compound shows a maximum on the liquidus curve at 27.5 mol.% HCl. However, we did not determine the pressure – temperature diagram and could not therefore take into account the amount of HCl remaining in the gas phase. Consequently, the true composition of the compound must correspond to a somewhat lower content of HCl. It is most probable that this compound has also the formula $HCl \cdot 3C_6H_5OH$. The chemical analysis of this compound, obtained by crystallization from melts greatly enriched in HCl at -100° and by then removing excess HCl at this temperature by pumping, showed 29 mol.% HCl. Hence, this method of establishing the formula of the compound is very approximate, since it gives no guarantee that excess of a component will not be retained, particularly when the compound is prepared at very low temperatures.

In order to show the analogies existing among substances that form compounds with phenol, it is of great interest to determine the heats of formation of these compounds from the gas and solid phenol. Having determined the dissociation pressures at various temperatures below the eutectic point, the heats of formation may be calculated by Clapeyron's formula:

$$Q = -R \cdot 2.303 \frac{d\log p}{d1/T}$$

where Q is the heat of formation in kcal per mole; R is the gas constant; p is the dissociation pressure; and T is the absolute temperature. The dissociation pressures of various compounds determined by us earlier [1] or in the present work are given in mm Hg in Table 3.

TABLE 3

Gas	Dissociation pressure of the gas in mm Hg at temperature:							
	-30°	-20°	-10°	0°	5°	15°	20°	25°
CO_2	240	437	770	1340	—	—	—	—
Xe	115	195	330	630	—	—	—	—
HCl	106	187	319	560	—	—	—	—
H_2S	35	60	108	198	—	449	580	750
HBr	29	50	91	160	—	362	475	621
SO_2	—	—	—	72	100	179	238	323

Forcrand [9] calculated the heats of formation of hydrates of gases by a modified Trouton formula: Q = 30T, where T is the absolute temperature at which the dissociation pressure reaches 1 atm.

In Table 4 we give the melting points of these compounds and the temperatures at which p = 1 atm; there follows the heats of formation, calculated according to Clapeyron and to Forcrand, and also the heats of formation of the corresponding hydrates, calculated by Forcrand.

TABLE 4

Gas	Temperature in °C		Heat of formation in kcal		
			Compounds with phenol		Hydrates, acc. to Forcrand
	of melting	at which P = 1 atm.	Acc. to Clapeyron	Acc. to Forcrand	
CO_2	45.4	-10.3	7.32	7.89	7.55
Xe	-	4.0	7.33	8.31	8.16
HCl	35.9	5.8	7.38	8.37	-
H_2S	47.4	25.3	8.45	8.94	8.20
HBr	-	28.5	8.50	9.04	-
SO_2	34.2	39.0	9.00	9.36	8.40

According to our measurements, the compound of krypton with phenol has a melting point of 47°. We were unable to determine the fusion diagram for the system xenon-phenol, owing to the very small amount of xenon that was available to us. The determination of fusion diagrams for the systems A- and Kr-phenol is very difficult, owing to the high pressures.

The results in Table 4 show that the heats of formation of these compounds are all very close to one another. The heats of formation of the compounds of phenol with H_2S and HBr, for which the molecular radii and Van-der-Waals forces are very similar, are almost identical.

For the compounds of H_2S, SO_2, and HCl with phenol we have established the formula 1 M: $3C_6H_5OH$. As the compounds of A, Xe, and Rn with phenol are isomorphous with the compounds of H_2S, SO_2, and HCl with phenol, they also must have the formula 1 M: $3C_6H_5OH$, which is confirmed also by the closeness of the values of heat of formation for the Xe, HCl, H_2S, and HBr compounds.

The close analogy in properties between the six compounds given in the table proves that their formation is brought about by the same type of chemical bond. For compounds of the inert gases, this bond can in the present case be only Van-der-Waals. Also, analogy between substances that are so different in the chemical sense can occur only when they enter in combination as whole molecules, which must have a definite resemblance to atoms of inert gases. The group of molecular compounds formed by phenon is evidently larger than that of molecular crystal-hydrates, for it includes also hydrogen halide compounds, which give hydroxonium compounds with water, and not crystal-hydrates. Compounds of this group are more stable than crystal-hydrates, for, at a coordination number of 3, they have almost the same heat of formation as the crystal-hydrates of coordination number 6.

SUMMARY

1. The compound of Rn with phenol is isomorphous with that of SO_2 with phenol. At 15°, the distribution constant of radon between the gas phase and the crystals of the SO_2 compound is 0.24. For the compound of H_2S with phenol, it is 1.24. Consequently, radon forms a phenol compound that is more stable than that of H_2S, and less stable than that of SO_2. The value of the dissociation pressure of the radon compound must lie between the values for the dissociation pressures of these latter compounds.

2. It is shown that the compounds of H_2S, SO_2, and HCl with phenol have the formula 1 M: $3C_6H_5OH$. The isomorphism of these compounds with compounds formed between the inert gases and phenol and the closeness of their heats of formation show that their formulas are analogous and that the same type of chemical bond is present.

V. G. Khlopin Radium Institute,
USSR Academy of Sciences

Received May 14, 1951

LITERATURE CITED

[1] B.A.Nikitin. Bull.Acad.Sci.USSR, Div.Chem.Sci. 1, 39 (1940).
[2] Terres and Vollmer, Petroleum Z. 31, 19 (1935).
[3] B.A.Nikitin. Proc.Acad.Sci.USSR, 24, No. 6, 567 (1939).
[4] B.A.Nikitin. Proc.Acad.Sci.USSR, 29, No. 8-9, 570 (1940).
[5] B.A.Nikitin, M.P.Kovalskaya, and M.F.Pushlenkov. Bull.Acad.Sci.USSR, Div.Chem.Sci., 6, 661 (1951).
[6] B.A.Nikitin, J.Gen.Chem., 9, 1167 (1939).
[7] V.G.Khlopin. Trans.Radium Inst., 4, 34 (1938).
[8] Meyer and Kolbe, J.prakt.Chem. 25, 462 (1882).
[9] R. de Forcrand, Ann.chim. 7, 384 (1903).

BLANK
PAGE

EXPERIMENTAL STUDY OF THE ELECTRON DENSITY IN CRYSTALS

COMMUNICATION 5. ELECTRON DENSITY OF Mg_2Si

N. V. Ageev and L. N. Guseva

The determination of the electron density in the lattice of the chemical compound Mg_2Si was carried out with the object of studying the character of the chemical linkage of the atoms in this compound. Mg_2Si is a member of the group of compounds formed by magnesium with elements of the fourth group: silicon, germanium, tin, and lead (Mg_2Si, Mg_2Ge, Mg_2Sn, and Mg_2Pb). The composition of these compounds is in accord with the usual rules of valency (the elements of the fourth group being here charged negatively); they all have the same crystal structure, anti-isomorphous to fluorspar, and they do not form solid solutions with their components, which is characteristic for ionic compounds. The physical properties of the compounds vary in regular manner as the atomic number of the anionic element is increased. For example, the melting point varies from 1102° for Mg_2Si to 780° for Mg_2Sn and 553° for Mg_2Pb, i.e., the stability of the compounds falls in this series. Affinity for electrons falls in the same sense, and the metallic properties of the anion elements become more marked. The electrical resistivity falls from $1096 \cdot 10^{-6}$ ohm/cm^3 for Mg_2Sn to $180 \cdot 10^{-6}$ ohm/cm^3 for Mg_2Pb (there are no data in the literature for Mg_2Si). An examination of these properties leads to the conclusion that the ionic character of the atomic linkage must be most pronounced in the compound Mg_2Si, and metallic character – in the compound Mg_2Pb [1].

A study of the distribution of electron density permits the character of the chemical linkage of the atoms in the lattices of chemical compounds of this group to be more fully elucidated. The compound chosen for examination is a very convenient one from the point of view of the technique of electron density determination. Both components of the compound Mg_2Si are comparatively light elements of low atomic number, and from the friable compound it is easy to prepare fine powders that are stable in air. The phase diagram for the system Mg_2Si has been studied, and it has been shown that Mg_2Si is the only compound formed in this system and that it forms two eutectics with its components [2]. This compound does not form solid solutions.

EXPERIMENTAL

Preparation of the sample

An alloy corresponding to the chemical compound Mg_2Si was obtained by melting together magnesium and silicon in silica crucibles in a high-frequency furnace. First of all the silicon was melted (for this purpose the silica crucible was placed inside a graphite one), then the magnesium was added. A series of alloys of varying magnesium content were prepared. After preparing the alloys, they were annealed at 1000° for three days, and their microstructure was examined. On the basis of the results, the alloy was selected that was nearest in composition to the compound Mg_2Si, and it was analyzed for its magnesium content. The composition of the chosen alloy corresponded to a magnesium content of 63.34% by wt., the theoretical magnesium content for the compound Mg_2Si being 63.4% by wt. The experimentally determined lattice constant of the chemical compound is 6.338 ± 0.001 Å. This value of the constant differs from that obtained by Owen and Preston [3] and is in good agreement with the value obtained by Klemm and Westling [4]. Measurements of the lattice constants for alloys with an excess of one component above the stoichiometric proportion did not show any variation in the lattice constant of the chemical compound Mg_2Si, which points to the nonformation of solid solutions in the chemical compound.

The alloy corresponding to the chemical compound is very friable and has a blue color with a metallic luster. The powder for the preparation of the sample was ground up in a mortar, grinding being continued until continuous lines were formed on the X-ray photographs with sharp resolution of the α-reflection doublets of the higher orders.

Preparation of the X-ray photographs and their photometry

The procedure for the preparation of the X-ray photographs was the same as that used by us previously [5]. They were obtained with copper radiation and a nickel filter, using plane and cylindrical samples. The latter served mainly for the determination of the intensity of the weak lines. The absorption of the cylindrical samples could not be taken into account because of the low values of the absorption coefficients of the scattering atoms, the small diameters (about 0.2-0.3 mm) of the samples, and the close reflection angles for the lines on the X-ray-gram that were to be compared. For the flat samples, the absorption was calculated by the formula:

$$A = \frac{\sin(2\theta - \alpha)}{\sin\alpha + \sin(2\theta - \alpha)},$$

where α is the angle between the incident ray and the plane of the sample (varying from 15 to 50°).

As the compound Mg_2Si gives rise to reflections that vary considerably in intensity [thus for planes for which $h + k + l = 4n$, $\Sigma = 4(Si + 2Mg)$; when $h + k + l = 4n \pm 1$, $\Sigma = 4Si$; and when $h + k + l = 4n \pm 2$, $\Sigma = 4(Si - 2Mg)$], it was essential to prepare a series of X-ray photographs of varying exposure. In cases where β lines fell on α lines and there was the possibility of the first passing through the nickel filter, attention was turned to the absence of β lines from the planes having the most intense reflection.

The photometry of the X-ray diagram was carried out at a magnification of 1:6. When the X-ray diagrams were prepared from flat samples, the determination of the intensity was made from the area of the peak on the photometric curve, which was determined, as previously, by weighing the peak, after redrawing on a logarithmic scale. The limit of the linear dependency of blackening on the X-ray intensity was verified for the film used. Blackening values exceeding the linear limit were not used for calculation purposes. The blackening of the ground of the X-ray photograph was taken into account also.

Determination of the absolute values of the atomic factor

Conversion from relative to absolute values of the atomic scattering factor was carried out with the aid of aluminum as a standard. The X-ray diagrams were prepared by the substitution method, using equal exposures for aluminum and for the compound Mg_2Si. The comparison was carried out for reflections from planes (331) and (422) of aluminum and (620) and (642) of the compound Mg_2Si. The values for the atomic factors of aluminum obtained by James, Brindle, and Wood [6] were taken as standard.

The calculation was performed by the formula:

$$F_{1abs.} = \frac{f_1\ rel.}{f_2\ rel.} \cdot \frac{N_2}{N_1} \sqrt{\frac{\mu_1 t_2}{\mu_2 t_1}}\, F_{2abs.} ,$$

where the subscript (1) relates to data for Mg_2Si and the subscript (2) to data for aluminum. All the symbols have their usual significance, and

$$\underline{N} = 1/\underline{V} = 1/a^2,$$

For Mg_2Si, $\underline{a}$ = 6.338 A; and for aluminum, $\underline{a}$ = 4.041 A. The exposure ratio $\underline{t}_2:\underline{t}_1$ = 1:1. For aluminum in copper radiation, $\mu = 131.5$; for the compound Mg_2Si in copper radiation, μ was calculated according to the formula:

$$\left(\frac{\mu}{\rho}\right)_{Mg_2Si} = 0.366\left(\frac{\mu}{\rho}\right)_{Si} + 0.634\left(\frac{\mu}{\rho}\right)_{Mg} = 47.81$$

whence $\mu_{Mg_2Si} = 47.81 \times 2 = 95.62$, since the density of Mg_2Si determined from the X-ray-structure results has the value 2.00; the pycnometrical value is 2.01. The values of $\frac{\mu}{\rho}$ for magnesium, aluminum, and silicon are taken from the reference literature [7].

Inserting the calculated values into the equation already cited, we obtain:

$$\underline{F}_{abs._{Mg_2Si}} = \underline{F}_{abs._{Al}} \cdot 3.29 \frac{\underline{f}_{rel._{Mg_2Si}}}{\underline{f}_{rel._{Al}}}$$

The comparisons were made in pairs - for planes (331) aluminum and (620) Mg_2Si, and (422) aluminum and (642) Mg_2Si. The determination of the factor for converting relative into absolute atomic factors was carried out on the basis of the results of three determinations. The results of these determinations are given in Table.1.

TABLE 1

Conversion of relative values of the structural factor into absolute values

No. of determination	Results for aluminum				Results for Mg_2Si			
	hkl	I/A	$\underline{f}_{rel.}$	$\underline{F}_{abs}$	hkl	I/A	$f_{rel.}$	$\underline{F}_{abs.}$
1	422	391	2.70	4.16	620	319	3.12	13.18
	331	374	3.24	3.29	642	590	2.44	10.16
2	422	282	2.29	4.16	620	193	2.43	12.52
	331	251	2.65	3.29	642	382	1.97	9.63
3	331	415	3.41	4.16	620	346	3.25	13.04

Mean value: $F_{abs.620} = 12.91$; $F_{abs.642} = 9.90$.

The results in this table served further for the conversion of the relative atomic factors into absolute. The dispersion correction was made from Hönl's results [8].

TABLE 2

Determination of the absolute values of F for the compound Mg_2Si

hkl	sin θ	sin θ/λ	$F_{\lambda Cu}$ rel.	$F_{\lambda Cu}$ abs.	e^{-M}	$\Delta f \cdot e^{-M}$	F_{020} abs.
111	0.210	0.136	59.5	10.33	0.957	0.17	10.16
200	0.243	0.158	42.5	7.38	0.943	0.11	7.27
220	0.343	0.223	130.0	22.58	0.889	0.43	22.15
311	0.403	0.262	45.5	7.90	0.850	0.15	7.75
222	0.420	0.273	31.7	6.43	0.838	0,10	6.33
400	0.485	0.315	115.4	20.04	0.790	0.38	19.66
331	0.529	0.344	40.7	7.07	0.756	0.14	6.93
420	0.543	0.353	28.5	4.95	0.745	0.09	4.86
422	0.595	0.386	100.1	17.37	0.702	0.34	17.03
511(333)	0.631	0.410	36.0	6.25	0.672	0.12	6.13
440	0.687	0.446	85.6	14.87	0.624	0.30	14.57
531	0.718	0.466	31.2	5.42	0.597	0.11	5.31
600(442)	0.728	0.473	–	3.50[1]	0.588	0.07	3.43
620	0.768	0.499	74.2	12.89	0.577	0.28	12.61
533	0.796	0.517	–	5.00[1]	0.531	0.10	4.90
622	0.805	0.523	–	2.80[1]	0.523	0.06	2.74
444	0.841	0.546	66.3	11.52	0.493	0.24	11.28
711(551)	0.867	0.563	24.6	4.27	0.472	0.08	4.19
640	0.875	0.569	–	2.40[1]	0.465	0.06	2.34
642	0,908	0.590	57.0	9.90	0.438	0.21	9.69

[1] Values obtained by graphical interpolation.

Results for the determination of F-values for the compound Mg_2Si are given in Table 2. In the graph (Fig. 1) F_{020} is given in absolute units for a temperature of 20°, and curves are given, according to the various planes, of $F = 2\underline{f}_{Mg} + \underline{f}_{Si}$, $F = \underline{f}_{Si}$, $F = \underline{f}_{Si} - 2\underline{f}_{Mg}$.

Calculation of the characteristic temperature

There are no data in the literature concerning the characteristic temperature of Mg_2Si, and this quantity was determined by calculation from Lindeman's equation, which involves the melting point [9]. The characteristic temperature;

$$\Theta = c\sqrt{T_s/a\underline{v}^{2/3}},$$

where $\underline{a}$ is the atomic weight, $\underline{v}$ the atomic volume, $\underline{T}_s$ the absolute temperature at the m.p., and $\underline{c}$ is a constant, taken to be 137. For the calculation of the characteristic temperature of Mg_2Si, the following values were assumed; M.p. 1373°K, atomic volume of magnesium 14.1 and of silicon 12.0, mean atomic weight 25.57. From these data the characteristic temperature of Mg_2Si was calculated to be 423°.

Calculation of the temperature factor

When introducing the dispersion correction, the temperature factor is calculated from the formula:

$$F_1 = F_0 \cdot e^{-\beta_t h^2} = F_0 \cdot e^{-M},$$

where

$$M = \frac{6h^2}{mk\theta}\left[\frac{\Phi(x)}{x} + \frac{1}{4}\right]\frac{\sin^2\theta}{\lambda^2}.$$

Here the following values are assumed for the constants:

$$h = 6.55 \cdot 10^{-27}; \quad m_n = 1.662 \cdot 10^{-24}; \quad k = 1.371 \cdot 10^{-16}.$$

When recalculating the absolute values of the atomic factors, obtained for 20°, for higher temperatures in order to establish convergency of the Fourier series, the following formula was used:

$$F_1 = F_{20} \cdot e^{-\beta_t h^2},$$

where

$$\beta = \frac{6h^2}{mk\theta}\left\{\frac{\Phi\left(\frac{\theta}{T}\right)}{\frac{\theta}{T}} - \frac{\Phi\left(\frac{\theta}{T_{20}}\right)}{\frac{\theta}{T_{20}}}\right\}.$$

The assumed values of the constants were the same as before.

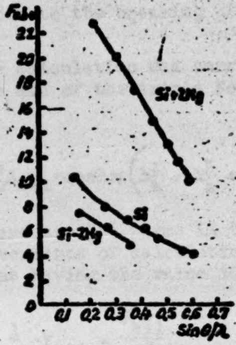


Figure 1. The F-curve for the compound Mg_2Si.

Calculation of electron density

The calculation of electron density was carried out for a temperature of 4800°K. Atomic factor values for this temperature are given in Table 3.

TABLE 3

Atomic factors recalculated for a temperature of 4800°K

hkl	F_{o20} abs.	e^{-M}	F_{4800}
111	10.16	0.802	8.14
200	7.27	0.745	5.42
220	22.15	0.555	12.30
311	7.75	0.445	3.45
222	6.33	0.414	2.62
400	19.66	0.308	6.06
331	6.93	0.247	1.71
420	4.86	0.230	1.12
422	17.03	0.171	2.91
511(333)	6.13	0.137	0.84
440	14.57	0.095	1.38
531	5.31	0.077	0.41
600(442)	3.43	0.071	0.24
620	12.61	0.053	0.06
533	4.90	0.042	0.21
622	2.74	0.039	0.11
444	11.28	0.029	0.33
711(551)	4.19	0.023	0.10
640	2.34	0.022	0.05
642	9.69	0.016	0.16

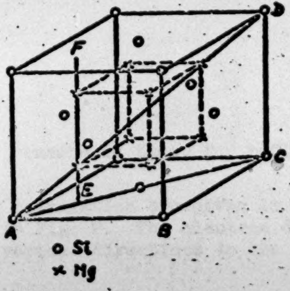


Figure 2. Unit cell of the compound Mg_2Si.

The minimum value of the atomic factor used in the calculation is about 2% of its value at 20°, and is not outside the limits of the accuracy of measurement. At the calculation temperature indicated, the distribution of electron density in the interionic space is free from any effect due to the breaking off of the series.

TABLE 4

Electron density in the [100], [110], [111] and $[001]_{3/4\,3/4}$ directions of the unit cell of the compound Mg_2Si

Distance in Å	Electron density in el./Å^3	Distance in Å	Electron density in el./Å^3
a) [100]–AB		c) [110]–AC	
0.00	10.53	0.00	10.53
0.63	2.75	0.45	4.67
1.27	0.36	0.90	1.06
1.58	0.22	1.34	0.32
1.90	0.09	1.79	0.19
2.54	0.06	2.24	0.19
3.17	0.00		
b) [111]–AD		d) $[001]_{3/4\,3/4}$–EF	
0.00	10.53	0.00	0.20
0.55	3.56	0.32	0.60
1.10	0.54	0.63	0.75
1.37	0.33	0.95	2.49
1.48	0.28	1.27	6.59
1.54	0.22	1.58	2.49
1.59	0.21	1.90	0.75
1.65	0.50	2.54	0.60
2.20	3.15	3.17	0.20
2.7	6.59		
3.30	3.13		
3.85	0.41		
4.40	0.10		
4.95	0.00		
5.50	0.00		

The calculation was carried out with the aid of the triple Fourier series:

$$\rho = \sum_{-\infty}^{+\infty}\sum\sum A_{hkl}\cdot\cos 2\pi\left(h\frac{x}{a} + k\frac{y}{a} + l\frac{z}{a}\right).$$

There are 536 terms in the series. For convenience of calculation we shall take a as having the value 10, and since

$$A_{hkl} = \frac{1}{v}\cdot F_{hkl} = \frac{F_{hkl}}{a^3},$$

therefore

$$\rho = A_0 + \frac{4}{a^3}\left\{F_{hkl}\cdot\cos 2\pi\left(h\frac{x}{10} + k\frac{y}{10} + l\frac{z}{10}\right)\right\}$$

and for $A_0 = \frac{4Si + 8Mg}{a^3}$ we have

$$\rho = 0.5965 + $$

$$+ 0.0157\left\{F_{hkl}\cdot\cos 2\pi\left(h\frac{x}{10} + k\frac{y}{10} + l\frac{z}{10}\right)\right\}.$$

In making the calculation it must be remembered that, for reflections for which $h + k + l = 4n \pm 2$, F is negative.

Results of the electron density calculation are given in Table 4. The directions for the calculation are shown in Fig. 2. The electron density results are shown graphically in Fig. 3 for the various directions in the unit cell, and in Fig. 4 for the (110) plane.

DISCUSSION OF RESULTS

The electron density calculations showed that the electron density in the lattice of the compound Mg_2Si has an irregular distribution. The interionic electron density in the (100) direction between the silicon ions (Fig. 3a) falls to zero, indicating absence of conductivity electrons within the limits of the electron density calculations. In the (110) direction there is a higher electron density, 0.2 el./Å^3 (Fig. 3b), which is to be attributed to homopolar bonds between these atoms. Similar electron density values are observed between the magnesium ions and between the ions of magnesium and silicon (Fig. 3c, 3d, and 4).

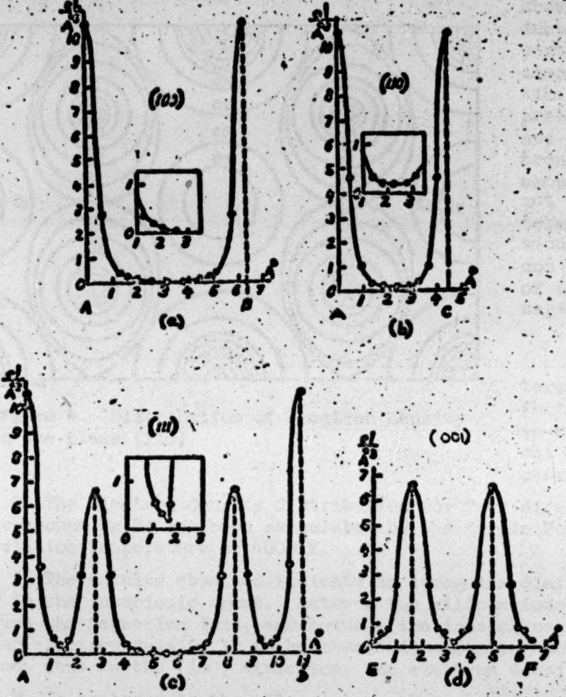


Figure 3. Electron density distribution in the directions: (a) (100)-AB; (b) (110)-AC; (c) (111)-AD; (d) $(001)_{3/4\,3/4}$-EF.

The electron density distribution around the magnesium ion has an asymetrical appearance contrasting with that around the silicon ion (Fig. 4).

On the basis of an examination of the crystal structure, physical properties, and positions of the elements in the periodic system for the series of compounds,

Mg_2Si, Mg_2Ge, Mg_2Sn, Mg_2Pb, the intermediate character of the chemical bond in this group of compounds - intermediate between ionic and metallic - was pointed out. The compound Mg_2Si is the extreme member of this group of chemical compounds and should, according to its position and properties, show ionic character in the bonds between its atoms to a considerable extent [1]. The electron density determination has shown that, as expected, conductivity electrons are absent in the lattice of the compound, while, at the same time, there are homopolar bonds present between the atoms, which are revealed by the higher electron density between the atoms, amounting to 0.2 el./Å^3. It was not considered possible to determine the degree of ionization of the magnesium and silicon atoms, owing to the absence of a sharp boundary between the separate ions.

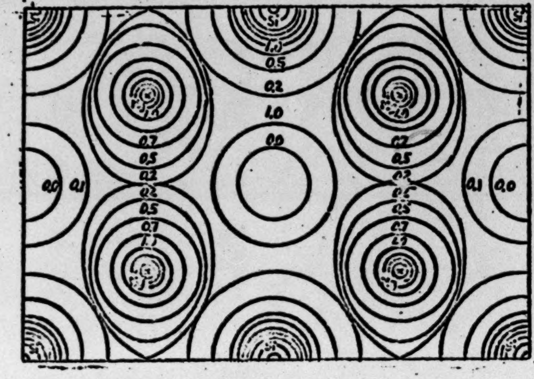


Figure 4. Distribution of electron density in the plane (110).

SUMMARY

1. The experimental determination of the structural factors for an alloy, close in composition to the chemical compound Mg_2Si, has been carried out.

2. The electron density distribution for four directions of the unit cell of the compound Mg_2Si has been calculated by the triple Fourier series method at a calculation temperature of 4800°K.

3. The results obtained indicate an irregular distribution of electron density in the interionic space. Between the silicon ions in the (110) direction, between the magnesium ions, and between the ions of magnesium and silicon, a higher electron density is to be observed, amounting to 0.2 el/Å^3. Between the silicon ions in the (100) direction, the electron density falls to zero.

4. In contrast to the silicon ion, the magnesium ion has an asymmetrical appearance with respect to electron density distribution.

5. The higher electron density between the atoms points to bhe presence of homopolar links in the lattice of the compound. The zero electron density in certain parts of the lattice points to the almost complete absence of conductivity electrons.

N.S.Kurnakov Institute of General
and Inorganic Chemistry of the
USSR Academy of Sciences

Received July 13, 1951

LITERATURE CITED

[1] N.V.Ageev. Nature of the Chemical Bond in Metallic Alloys. Moscow-Leningrad, USSR Acad.Sci.Press, 1947.

[2] M. Hansen. Structure of Binary Alloys, Vol. 2, 832, State Inst.Tech., 1941.

[3] E.A.Owen and G.D.Preston. Proc. Phys.Soc., 36, 343 (1924).

[4] W. Klemm and H. Westlinning. Z.anorg.allg.Chem., 245, 365 (1941).

[5] N.V.Ageev and D.L.Ageeva. Bull. Acad. Sci. USSR, Div. Chem.Sci., 1, 17 (1949); 3, 273 (1948); N.V.Ageev and L.N.Guseva. Ibid., 5, 470 (1948), 3, 225 (1949).

[6] R.W.James, G.W.Brindley and R.G.Wood. Proc. Roy. Soc. 125 (A), 401 (1929).

[7] Reference Book on X-ray Structure Analysis. Ed. by A.I.Kitaygorodsky, 1940.

[8] H. Hönl. Ann. Phys. 18, 651 (1933).

[9] F.A.Lindeman. Phys. Z., 11, 609 (1910).

BLANK
PAGE

KINETICS OF THE POLYMERIZATION OF COMPOUNDS CONTAINING A CONJUGATED LINK

POLYMERIZATION OF METHYL ACRYLATE

P. S. Shantarovich

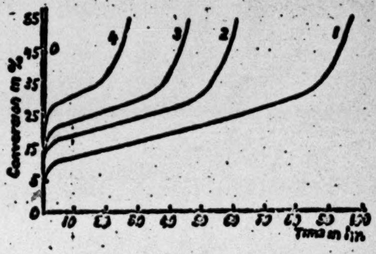
In the previous paper [1] the kinetics of the polymerization of chloroprene were described. It was then pointed out that the concept that we have developed concerning the polymerization of chloroprene may be extended also to other compounds, in fact to those which contain a conjugated link. In this paper we describe results on the kinetics of the polymerization of methyl acrylate in the mass (undiluted liquid), working at high degrees of conversion. The kinetics for a low degree of conversion into polymer (3-4%) have been studied by Bagdasaryan [2].

EXPERIMENTAL

Experimental Results

The experimental arrangement and the initiation conditions were similar to those used in the investigations on the polymerization of chloroprene. The reaction was initiated by light from a mercury lamp. Chemically active radiation (λ = 303-313 mμ) was filtered off by means of a 1.5-cm layer of 0.0005 M-K_2CrO_4. The reaction rate was measured by a dilatometric method. On illuminating the reaction vessel, polymerization did not begin immediately, but after a certain delay (about 1.5 min), it then proceeded at constant rate. An appreciable increase in rate was to be observed at 8-10% conversion, and at $X \approx 35\%$ the reaction went over into the stage of rapidly increasing rate. When the light is switched off, intense dark polymerization is to be observed, and it proceeds at a dwindling rate and, after a certain time, this attains a minimum value. The rate then increases very slowly as polymer is formed right until a nucleus of the insoluble form of the polymer arises in the polymerizing mass. The formation of nuclei of the opaque granular mass of polymer proceeds at various points in the reacting space. The formation of the nuclei, as regards number and the places at which they form, proceeds in an irregular fashion, but the moment at which nuclei arise is determined by the degree of conversion: when the reaction has proceeded to the extent of about 30-33%, nuclei appear. From this moment, the rate of polymerization sharply increases. The general kinetic picture of the dark polymerization of methyl acrylate is presented in Figure 1, beginning from the moment of switching off the light. The curves 1, 2, 3 and 4 were obtained after 10, 19, 24, and 32 min. irradiation of the polymerizing mass; at the end of this period the light was switched off. The amounts of polymer formed up to the moment when the light was switched off are respectively 7.5, 14, 18, and 24.5%. The further the photoreaction has gone, the shorter the period of the slow dark reaction. Thus, the kinetics of the formation of polymethyl methacrylate are precisely similar to those described by us previously [1] for the polymerization of chloroprene, though with this difference, that the point for the transition of the slow dark reaction into the non-stationary condition lies at about 31-32% conversion, instead of at 9-10% for chloroprene. Also, in contrast with the chloroprene polymerization, the character of the curves for the dark polymerization of methyl acrylate does not depend on the extent of the photo-reaction (i.e. on X_{phot}). All the curves can be fully superimposed. In all cases the same end-product is formed.

Fig. 1. Kinetics of the dark polymerization of methyl acrylate at 20°: 0) photo-reaction; 1) t_e 10 min., X_{phot} 7.5%; 2) t_e 19 min., X_{phot} 14%; 3) t_e 24 min., X_{phot} 18%; 4) t_e 32 min., X_{phot} 24.5%.



This particular circumstance permitted the observance of an essential fact, the observance of which was impossible in the polymerization of chloroprene;1) namely that the minimum rate (v_{min}) of the dark polymerization depends on the value of X_{phot} – the amount of polymer formed at the moment when the light is switched off, or, what amounts to the same, on the value of X_{min} – the amount of polymer formed at the moment when the dark reaction reaches the minimum rate.

From these results it is evident that the minimum rate may be expressed by the formula:

$$v_{min} = ZX^{n}_{min}. \tag{1}$$

X_m in mol.	$v_{min} \cdot 10^{-6}$ mol./sec·cm^3	
	Calculated	Found
0.00295	0.0077	0.0077
0.00473	0.0102	0.0098
0.0058	0.1010	0.0109
0.0079	0.0130	0.0127

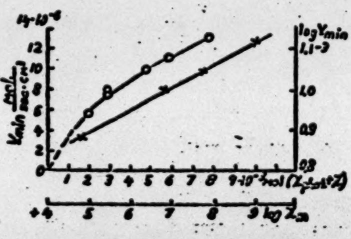


Fig. 2. Dependence of the minimum rate of the dark polymerization on the amount of polymer at the moment of minimum rate.

---

1) Because of the superposition of the process of ω-formation on the preceding process of μ-polymerization.

This relation is shown on Fig. 2, and in this figure is shown also the relation between log $\underline{v}_{min}$ and log X_{min}, whence we find that $\underline{n} = 0.53$ and $Z = 1.42 \cdot 10^{-7}$. Hence, the exact expression for the minimum rate has the form:

$$\underline{v}_{min} = 1.42 \cdot 10^{-7} \sqrt{X_m} \, . \tag{2}$$

Formula (2) corresponds closely to the experimental observations.

Discussion of Results

Switching off the light, i.e. curtailing the formation of active centers from outside, does not result in the complete stoppage of the polymerization of methyl acrylate. The reaction, having reached a certain minimum rate, continues to develop. In conformity with the chain-branching nature of the process, the change in the number of active centers (growing chains) with time may be represented by the equation:

$$\frac{dn}{dt} = \underline{f}n - k_5 n^2 .$$

After transformation and integration we find that the rate as a function of the X-quantity of forming polymer tends to a constant value:

$$\underline{v}_{min} = \frac{k_4 f}{k_5} \tag{3}$$

The experimental value of the minimum rate is given by Formula (2), and therefore

$$\frac{k_4 f}{k_5} = 1.4 \cdot 10^{-7} \sqrt{X_m} \, , \tag{4}$$

i.e. the minimum rate, which is determined by the concentration of centers $\underline{n} = \frac{f}{k_5}$, rises, with the extent of polymerization proportional to the root of the quantity of polymer that has been formed.

The relation (4) is possible only under the condition that: $k_5 = \frac{k_0}{\sqrt{X_m}}$, (5)

for neither the rate of chain growth nor the branching of the chains is determined by the amount of polymer that has been formed.

Hence, the kinetics of the slow dark reaction, which we regard as the reaction of the formation of the three-dimensional structure of the polymer, must be described by the differential equation:

$$\frac{dn}{dt} = fn - k_0 X^{-1/2} n^2 . \tag{6}$$

Integrating Equation (6) and assuming that $\frac{k_4 f}{k_0} = 1.42 \cdot 10^{-7}$, the rate of formation of the insoluble form of the polymer of methyl acrylate can be calculated, using the kinetic curves for the polymerization (Fig. 1). The result of the exact calculation is shown in Fig. 3 (broken lines). The photo-reaction ($\underline{v}_{phot}$) is represented by a curve that proceeds from the origin; $\underline{v}_{phot}$ in the stationary phase of the reaction has a value of $1.38 \cdot 10^{-6}$ mol./sec·cm³. Switching off the light (arrow) causes a fall in rate, which evidently results from a recombination of chains in the mass of the liquid phase. The process proceeds in space by a branching out of the polymer structure. As this structure develops, the rate of the curtailment of growing chains varies according to the law $k_5 X^{1/2} = \text{const}$. The broken curves in Fig. 3 demonstrate the accuracy with which this relationship holds.

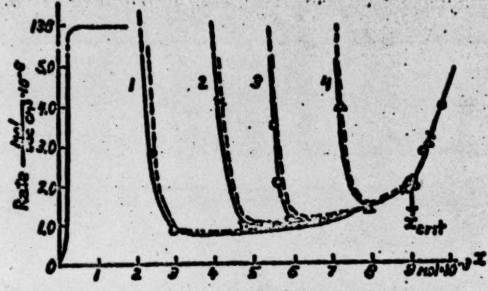


Fig. 3. Rate of the dark polymerization of methyl acrylate: 1) X_{phot}7.5%; 2) X_{phot}14%; 3) X_{phot}18%; 4) X_{phot}24.5%

SUMMARY

1. It is shown that the mechanisms of the polymerization of methyl acrylate and of chloroprene are of the same type, i.e. that of compounds that contain a system of conjugated bonds. The resemblance between the two processes is emphasized by the heats of the reaction, which are equal (18.7 kcal) [3]. The magnitude of the heat effect is to be related to the loss of the energy of conjugation in the original monomer when the system is transformed from the initial ($\underline{R}_n$ + $\underline{M}$) into the final ($\underline{R}_n$ + 1) state.

2. A differential equation describing the kinetics of the formation of the branched three-dimensional polymer structure has been obtained.

Institute of Chemical Physics
of the USSR Academy of Sciences

Received March 7, 1951

LITERATURE CITED

[1] P.S.Shantarovich and S.S.Medvedev. J. Phys. Chem., 21, 1143 (1947).

[2] Kh.S.Bagdasaryan. J. Phys. Chem., 22, 1181 (1948).

[3] L. Tonga, W.Kenyon. J. Am. Chem. Soc., 69, 2245 (1947).

INVESTIGATION OF SOLUBILITY IN THE RECIPROCAL SYSTEM

$CaSO_4 - KCl - H_2O$ AT 55°.

V.N. Sveshnikova

By a study of solubility in the quaternary reciprocal system $[CaSO_4 + 2KCl \rightleftarrows K_2SO_4 + CaCl_2] - H_2O$ at 55 and at 25° by the isothermal method it has been possible to establish the composition of the solid phases formed as a result of double-decomposition reactions and to give an explanation of the origin of the calcium chloride found in certain brines. The reaction that lies at the basis of the reciprocal system is accompanied by the formation of the double salt syngenite, $CaSO_4 \cdot K_2SO_4 \cdot H_2O$ [1]:

$$2CaSO_4 \cdot 2H_2O + 2KCl = CaSO_4 \cdot K_2SO_4 \cdot H_2O + CaCl_2 + 3H_2O.$$

It should be noted that a similar interaction between sodium chloride and calcium sulfate is not observed [2].

The reciprocal system $CaSO_4 - KCl - H_2O$ includes the following four ternary systems: 1) $KCl - CaCl_2 - H_2O$; 2) $CaSO_4 - CaCl_2 \quad H_2O$; 3) $K_2SO_4 - CaSO_4 - H_2O$; 4) $K_2SO_4 - KCl - H_2O$.

Ternary System $K_2SO_4 - CaSO_4 - H_2O$ at 55°

The ternary system potassium sulfate—calcium sulfate—water has been studied by many authors over a wide interval of temperature. Isotherms for 40, 60, and 100° were obtained by Hill [3]. This author carries out a detailed study of this system and gives its polytherm. In his investigations, Hill [3] takes up a critical attitude towards the work of van't Hoff on the determination of the transition points in the system calcium sulfate—water, and he gives 42° as the temperature for the transition gypsum—anhydrite, i.e., 21° lower than that found by van't Hoff (63°) [8]. Potassium sulfate lowers the solubility of calcium sulfate, and two double salts are formed: syngenite, $K_2SO_4 \cdot CaSO_4 \cdot H_2O$ and potassium pentacalcium sulfate, $5CaSO_4 \cdot K_2SO_4 \cdot H_2O$. In view of the long time required for establishment of equilibrium in systems containing calcium sulfate, the study of solubility was carried out using already prepared solid phases, i.e., an artificially prepared salt or mixture of salts was mixed in a vessel, and a liquid phase of known concentration was poured in. The solutions were allowed to stand in a thermostat for 8-10 days. The solid phases were identified by optical examination of the crystals. K, Ca, and SO_4 were determined in the liquid phase by the usual gravimetric methods. The results of the experiments are given in Table I. The solubility diagram consists of four branches (Fig. 1). The branch AB, which corresponds to the solubility of anhydrite $CaSO_4$, is lowered somewhat under the influence of potassium sulfate K_2SO_4. The branch BC, within the limits of 4-6% K_2SO_4, corresponds to the solubility of potassium pentacalcium sulfate,

$5CaSO_4 \cdot K_2SO_4 \cdot H_2O$; the branch CD to syngenite, $K_2SO_4 \cdot CaSO_4 \cdot H_2O$. The composition at all the points given on the diagram was obtained experimentally, with the exception of the point for the simultaneous crystallization of anhydrite and pentasulfate, which was obtained graphically and verified synthetically. The lines joining the points for the compositions of the double salts (syngenite and pentasulfate) to the origin do not pass through the corresponding crystallization branches; hence, both salts dissolve incongruently.

TABLE 1

Solubility isotherm at 55° for the system $K_2SO_4 - CaSO_4 - H_2O$

No.	Liquid phase (wt.%)					Solid phase (by optical examination of crystals)	Duration of expt. in days
	$K^{\cdot}$	SO_4''	$Ca^{\cdot\cdot}$	K_2SO_4	$CaSO_4$		
1	-	-	0.054	-	0.183	Anhydrite	8
2	0.56	0.81	0.036	1.30	0.129	Anhydrite	22
3		5.42	0.012	9.83	0.033	Syngenite	15
4	2.26	2.84	0.032	5.02	0.108	Pentasulfate	16
5	6.76	8.32	0.005	15.09	0.007	Syngenite + K_2SO_4	13
6	2.69	3.25	0.028	5.92	0.095	Pentasulfate + syngenite	26
7	1.19	1.62	0.035	2.94	0.125	Anhydrite	20
8	1.93	-	0.032	4.20	0.120	Anhydrite + pentasulfate	20

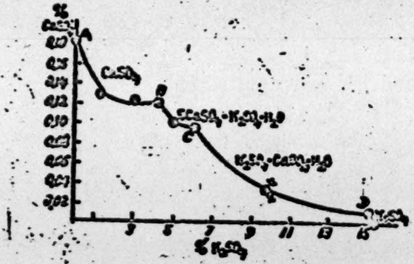


Fig. 1. Solubility isotherm at 55° for the system $K_2SO_4 - CaSO_4 - H_2O$

The formation of pentasulfate (Fig. 2) at this temperature from anhydrite, as also its decomposition into anhydrite, evidently proceeds through a stage in which syngenite is formed (microscopical observations).

The crystal-optical constants of syngenite are

$Ng = 1.518$; $Nm = 1.517$; $Np = 1.501$

The crystal-optical constants of potassium pentacalcium sulfate are

$Ng = 1.568$; $Nm = 1.569$; $Np = 1.556$ (Lyashenko).

Ternary system $CaSO_4 - CaCl_2 - H_2O$ at 55°

This system was studied at 55° both in the stable and in the metastable state (Fig. 3). The metastable diagram consists of the solubility branches of dihydrate gypsum, $CaSO_4 \cdot 2H_2O$, α-hemihydrate, $\alpha\text{-}CaSO_4 \cdot {}^1/_2\,H_2O$, and calcium chloride dihydrate, $CaCl \cdot 2H_2O$ [9]. It is interesting to note that, under the influence of calcium chloride, the solubility of gypsum first falls from 0.2 to 0.02% $CaSO_4$, and then rises to 0.1%. It is difficult to say how this is to be explained.

The stable diagram consists of the solubility branch of anhydrite, $CaSO_4$, and that of calcium chloride dihydrate, $CaCl_2 \cdot 2H_2O$. At 55° the solubilities of gypsum and anhydrite do not differ greatly, and this explains the closeness of the branches for the stable and metastable phases. The high stability of the metastable forms of gypsum at this temperature should be noted (Table 2).

TABLE 2

Solubility isotherm at 55° for the system $CaCl_2 - CaSO_4 - H_2O$

No.	Liquid phase (wt. %)						Solid phase[1])
	$Ca^{\cdot\cdot}$	Cl'	SO_4''	$CaCl_2$	$CaSO_4$	H_2O	
1	2.82	5.26	0.102	8.23	0.102	91.67	Gypsum $CaSO_4 \cdot 2H_2O$
2	3.31	5.78	0.068	9.08	0.097	90.82	Gypsum $CaSO_4 \cdot 2H_2O$
3	4.85	8.66	0.053	13.55	0.075	86.38	Gypsum $CaSO_4 \cdot 2H_2O$
4	8.13	14.70	0.022	23.00	0.030	76.97	Gypsum $CaSO_4 \cdot 2H_2O$
5	9.78	17.52	0.015	27.08	0.020	73.97	Gypsum $CaSO_4 \cdot 2H_2O$
6	11.01	20.41	0.011	31.91	0.016	68.07	Gypsum $CaSO_4 \cdot 2H_2O$
7	15.35	27.35	0.043	42.50	0.061	57.44	Gypsum $CaSO_4 \cdot 2H_2O$
8	17.41	30.49	0.065	47.47	0.090	52.14	α-$CaSO_4 \cdot {}^1/_2\ H_2O$
9	18.23	32.14	0.029	50.45	0.040	49.51	α-$CaSO_4 \cdot {}^1/_2\ H_2O$
10	18.57	32.71	0.007	51.30	0.010	48.69	α-$CaSO_4 \cdot {}^1/_2\ H_2O$
11	20.45	36.38	0.022	56.94	0.030	43.03	$CaCl_2 \cdot 2H_2O$ α-$CaSO_4 \cdot {}^1/_2 H_2O$
12	3.04	5.73	0.050	8.42	0.075	91.51	Anhydrite
13	9.55	17.62	0.009	27.0	0.013	73.00	Anhydrite

[1]) The solid phase was determined crystallo-optically by Lyashenko.

Ternary System $KCl - CaCl_2 - H_2O$ at 55°

The system has been investigated by a number of authors at various temperatures. The various authors have held diverse opinions about the chemistry of the system. Thus there was the suggestion of the possibility of the existence of the compound $KCl \cdot CaCl_2 \cdot 6H_2O$, analogous to carnallite, which was made in the Trans. State Inst. Appl. Chem by Shoykhet and Lukyanova [4], who studied the system over a wide range of temperatures (from -10 to 130°) in connection with its application to the treatment of the mother liquors of chlorate manufacture for separation of calcium chloride. Later, Lightfoot [5] found a double salt of composition $2KCl \cdot CaCl_2 \cdot 2H_2O$ at 35 and 75°.

In 1950, Assarsson [6] again investigated the system in detail and gave its polytherm; with the aid of Schreinemakers' method, he succeeded in proving that the double salt obtained has the composition $CaCl_2 \cdot KCl$.

Dergunov and Bergman [7] found this double compound in melts of the salts. In our solubility investigation on the ternary system at 55°, we have established the existence of three crystallization branches: that of KCl, that of $CaCl_2 \cdot 2H_2O$, and that of the double salt, $KCl \cdot CaCl_2$ (Figure 4).

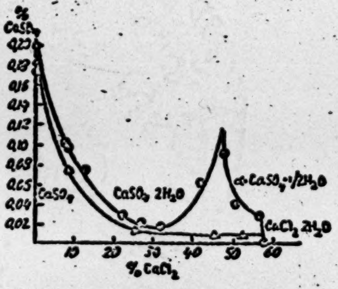


Figure 3. Solubility isotherm at 55° for the system $CaCl_2 - CaSO_4 - H_2O$.

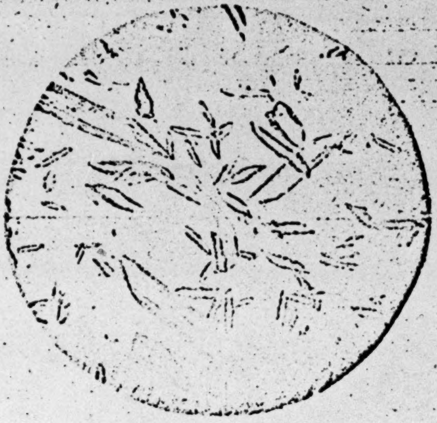


Fig. 2. Potassium pentacalcium sulfate $5CaSO_4 \cdot K_2SO_4 \cdot H_2O$. (x 250).

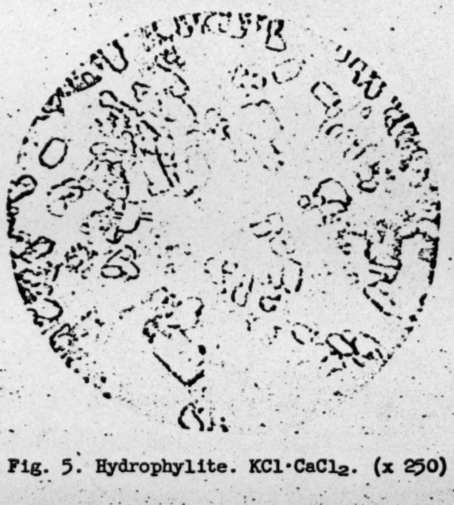


Fig. 5. Hydrophylite. $KCl \cdot CaCl_2$. (x 250)

TABLE 3

Solubility isotherm at 55° for the system KCl – $CaCl_2$ – H_2O.

No.	Liquid phase (wt. %)					Solid phase
	$Ca^{\cdot\cdot}$	$K^{\cdot}$	Cl'	$CaCl_2$	KCl	
1	19.98	2.43	37.51	55.26	4.63	$CaCl_2 \cdot 2H_2O$
2	20.37	2.34	37.90	56.40	4.46	$CaCl_2 \cdot 2H_2O$ + $KCl \cdot CaCl_2$
3	1.74	13.44	15.20	4.82	25.66	KCl
4	11.40	3.33	3.05	31.55	6.35	KCl
5	14.51	2.72	28.07	40.18	5.11	KCl
6	4.60	9.63	16.48	12.75	18.27	KCl
7	11.52	3.18	23.48	31.89	6.07	KCl
8	—	—	—	49.35	7.79	$KCl \cdot CaCl_2$; KCl

The double salt $KCl \cdot CaCl_2$, which was investigated crystallo-optically for the first time by Lyashenko, corresponds to the little studied natural mineral hydrophylite (Ng = 1.572, Np = 1.526) (Fig. 5). The temperature limits for the existence of $KCl \cdot CaCl_2$, according to the results of the last authors, are from 37.8° to fusion. The salt is difficult to separate because of the high viscosity of the solutions from which it is prepared. The results of the experiments are given in Table 3.

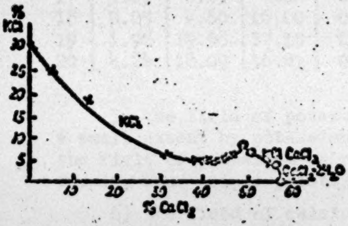


Fig. 4. Solubility isotherm at 55° for the system $CaCl_2$ – KCl – H_2O.

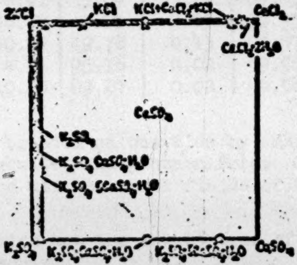


Fig. 6. Solubility isotherm at 55° for the system $CaSO_4$ – KCl – H_2O.

The Reciprocal System $CaSO_4$ – KCl – H_2O at 55°

The system was first studied by the author at 25° in 1947 [9]. At 55° the solubility diagram consists of the following fields (Figure 6):

1) the field of anhydrite $CaSO_4$, which occupies the greater part of the area – 96.50% of the whole area of the square;

2) the field of pentasulfate, which is immediately adjacent to the field of anhydrite: 0.66% of the whole area of the square;

3) the field of syngenite, which is between the fields of anhydrite and K_2SO_4;

4) the field of potassium sulfate, which is small in size and is adjacent, on the one side, to the field of syngenite, and on the other side – to the field of potassium chloride: 0.32%;

TABLE 4

Solubility isotherm at 55° for the reciprocal system $CaSO_4$ - KCl - H_2O

No.	Comp. of liquid phase in % by wt.					Comp. of liquid phase in ion-equiv.				
	K_2	Ca	Cl_2	SO_4	H_2O	K_2	Ca	SO_4	Cl_2	H_2O per 1000 ion-equiv.
1	2.34	20.37	37.90	—	39.39	5.56	94.44	—	100.00	4062.0
2	6.76	0.005	—	8.32	84.91	99.88	0.12	100.00	—	54.517
3	2.69	0.03	—	3.25	94.03	97.86	2.14	100.00	—	148.477
4	1.93	0.03	—	2.37	95.67	97.05	2.95	100.00	—	208.808
5	16.40	—	14.36	0.71	68.53	100.00	—	3.53	96.47	18.124
6	15.71	0.007	14.04	0.71	69.47	—	0.86	3.60	96.40	18.901
7	8.81	0.04	5.48	3.52	82.15	99.11	0.89	32.16	67.83	40.022
8	11.69	0.02	10.09	0.27	77.93	99.66	0.34	1.94	98.06	29.827
9	—	0.01	8.35	2.84	76.38	99.87	0.13	20.05	79.95	28.785
10	5.44	0.06	4.55	0.81	89.14	97.69	2.31	11.62	88.38	68.823
11	3.21	0.03	1.16	2.37	93.23	98.38	1.62	60.09	39.91	125.126
12	2.65	0.04	1.18	1.77	94.36	96.86	3.14	52.54	47.46	149.510
13	8.25	0.06	5.38	2.94	83.37	98.71	1.29	28.75	71.25	43.490
14	2.50	0.04	0.79	2.10	94.57	96.99	3.11	66.25	33.75	159.060
15	16.08	0.45	15.81	0.11	67.55	94.82	5.18	0.50	99.50	172.894
16	3.19	0.05	1.93	1.42	93.41	96.91	3.09	35.14	64.85	123.340
17	5.65	0.09	4.82	0.65	88.79	96.79	3.21	9.05	90.95	66.024
18	9.05	4.60	16.00	0.09	70.00	50.22	49.78	0.43	99.57	17.130
19	1.98	19.98	37.15	0.005	40.89	4.84	95.16	0.02	99.98	4.331
20	4.24	18.09	36.21	0.005	—	10.73	89.27	0.02	99.98	-

5) the field of potassium chloride, bounded on one side by anhydrite and to a small extent by potassium sulfate, syngenite, and pentasulfate: 0.50% (thus the field of potassium chloride borders on all the other fields of the system, forming four triple points):

6) the field of calcium chloride, which has the lowest area of all the fields: 0.03% of the whole area of the square;

7) the field of the double salt $KCl \cdot CaCl_2$, which borders on the KCl field, on the $CaSO_4$ field, and on the $CaCl_2 \cdot 2H_2O$ field.

Stable points of simultaneous crystallization within the system:

1. KCl; K_2SO_4; syngenite – composition in ion-%: 96.40 Cl_2; 3.60 SO_4; 0.86 Ca; 99.14 K_2.
2. KCl; syngenite; pentasulfate: 99.0 Cl_2; 1.0 SO_4; 88.0 K_2; 2.0 Ca.
3. KCl; pentasulfate; $CaSO_4$; 0.70 SO_4; 99.30 Cl_2; 3.3 Ca; 96.7 K_2.
4. $KCl \cdot CaCl_2$; $CaCl_2 \cdot 2H_2O$; $CaSO_4$; 0.70 SO_4; 99.3 Cl_2; 5.7 K_2; 94.3 Ca.
5. KCl; $CaCl_2 \cdot KCl$; $CaSO_4$; 7 fields of crystallization, 5 points denoting simultaneous crystallization of three phases, and 7 points denoting simultaneous crystallization of two phases. The fields within the system were delimited by the method of adding a third salt to the non-variant solutions of the ternary systems. The solutions were kept in a thermostat for 10-25 days. The average time required for establishment of equilibrium was 2 weeks, so long as the solution was stirred with the already prepared solid phases. At 55° equilibrium was established noticeably more rapidly than at 25°.

The reaction between calcium sulfate and potassium chloride in solution is usually accompanied by the formation, together with calcium chloride, of syngenite, whose solubility is less than that of anhydrite. This, of course, leads

TABLE 2 (continued)

Composition of solid phase	Time allowed for establishment of equilibrium (days)
$CaCl_2 \cdot 2H_2O$ + KCl	10
Syngenite + K_2SO_4	14
Pentasulfate + syngenite	14
Anhydrite + pentasulfate	14
KCl + K_2SO_4	14
Syngenite, KCl, K_2SO_4	10
Syngenite, K_2SO_4	25
Syngenite, KCl	45
Syngenite, K_2SO_4	21
Syngenite + pentasulfate	14
Syngenite	10
Anhydrite + pentasulfate	18
Syngenite	12
Pentasulfate	15
Anhydrite + KCl	
Anhydrite + Pentasulfate	18
Syngenite + Pentasulfate	8
Anhydrite + KCl	14
Anhydrite + $KCl \cdot CaCl_2$ + $CaCl_2 \cdot 2H_2O$	21
KCl + $KCl \cdot CaCl_2$ + $CaSO_4$	

to a displacement of the reaction from left to right.

The next stage of the reaction leads, under known conditions, to formation of pentasulfate $5CaSO_4 \cdot K_2SO_4 \cdot H_2O$. Whereas the formation of syngenite occurs over a wide range of temperature, from 0 to 100°, the formation of pentasulfate occurs at higher than 32° [8].

$$CaSO_4 \cdot K_2SO_4 \cdot H_2O + 4CaSO_4 = 5CaSO_4 \cdot K_2SO_4 \cdot H_2O.$$

On comparing the solubility diagrams for 55° with those for 25° [9], we are led to the conclusion that:

1. Rise in temperature has a negative action on the double-decomposition reaction between $CaSO_4$ and KCl, for the syngenite field shrinks relative to the other crystallization fields, and the solubility of syngenite therefore increases [9]. However, the solubility of anhydrite falls with rise in temperature, which confirms the view expressed earlier, that this reaction has a negative temperature coefficient.

2. The number of separate fields in the system increases as the temperature rises. At 25° the double salts, pentasulfate and hydrophylite, are absent [9].

3. At 25° the stable form of calcium sulfate is dihydrate gypsum, whereas at 55° it is anhydrite.

In order to see whether a double-decomposition reaction is possible between $CaSO_4$ and KCl in the solid state under the influence of pressure, the molecular volumes of the initial and final substances in the reaction $CaSO_4 + 2KCl \rightleftarrows K_2SO_4 + CaCl_2$ were calculated. The molecular volume calculation showed that increase in pressure should not favor the formation of calcium chloride and syngenite. Actually, experiments carried out with a hydraulic press, (using pressures of up to 20 T, confirmed the theoretical calculations:) no calcium chloride was formed in the mixtures subjected to pressure.

The facts obtained as a result of the study of the reciprocal system made an approach possible to the question of the formation of calcium chloride in natural brines. The occurrence of calcium chloride in natural lakes of the second class (Kurnakov's classification) is usually explained on the basis of the following double-decomposition reactions:

1) Kurnakov's reaction:

$$2Ca(HCO_3)_2 + MgCl_2 = CaCl_2 + CaMg(CO_3)_2 + 2H_2O;$$

2) the cation-exchange reaction:

$$Ca - \text{aluminum silicate} + MgCl_2 \rightleftarrows Mg - \text{aluminum silicate} + CaCl_2.$$

Urazov [11] investigated the Bakin lakes of the Apsheron peninsula and found them to contain a large amount of calcium chloride, reaching 12%. In the Perekop lakes of the Crimea, the $CaCl_2$ content is less and varies from 0.2 to 2.2%. Kurnakov [10] explains the excess calcium ion in the latter by the first double-decomposition reaction. In the Solikam salt deposits, potassium chloride is found in paragenesis with anhydrite. In his investigations of this deposit, Morachevsky [12] established the presence of calcium chloride to the extent of 0.3-3.3% in the zone of crystallization of potassium salts, but, as the author points out, no calcium chloride is found in the zone of crystallization of rock salt. Since the predominating calcium compound in this salt deposit is anhydrite ($CaSO_4$), the presence of calcium chloride in the zone of crystallization of potassium salts may be explained by the double-decomposition reaction:

$$2CaSO_4 + 2KCl + H_2O = CaSO_4 \cdot K_2SO_4 \cdot H_2O + CaCl_2,$$

which occurred during the drying-up of the Perm sea, when the salt layers of the Higher Kama deposits were formed.

Interaction between potassium chloride and anhydrite can give considerable amounts of calcium chloride. Thus, at point C on Figure 6, where we have simultaneous crystallization of potassium chloride and anhydrite, the calcium chloride content of the liquid phase is as high as 12%. As this reaction proceeds further at lower temperatures, the possibilities of its occurrence in nature are widened. Although other double-decomposition reactions cannot be excluded for the Solikam deposits, the above considerations are confirmed by the following:

1) the occurrence of paragenesis of potassium chloride with anhydrite;

2) the presence of calcium chloride in the zone of crystallization of potassium salts and its absence in the zone of crystallization of rock salt.

SUMMARY

1. A study has been made of the solubility relations at 55° in the reciprocal system:

$$[CaSO_4 + 2KCl \rightleftarrows K_2SO_4 + CaCl_2] - H_2O$$

and in the ternary systems:

$KCl - CaCl_2 - H_2O$; $CaSO_4 - CaCl_2 - H_2O$; $CaSO_4 - K_2SO_4 - H_2O$.

2. In the reciprocal system 7 fields of crystallization have been established, and of these 3 correspond to double salts: syngenite, $K_2SO_4 \cdot CaSO_4 \cdot H_2O$; potassium pentacalcium sulfate, $5CaSO_4 \cdot K_2SO_4 \cdot H_2O$; and hydrophylite, $KCl \cdot CaCl_2$.

3. The formation of calcium chloride proceeds owing to the formation of the difficultly soluble double salt, syngenite.

4. Lowering of temperature favors the double-decomposition reactions.

5. The occurrence of calcium chloride in the zone of crystallization of potassium salts in the Solikam deposits may be explained, as can also other metamorphization reactions, by the double-decomposition reaction studied.

Kurnakov Institute of General
and Inorganic Chemistry
USSR Academy of Science

Received July 7, 1951

LITERATURE CITED

[1] H. Struve. Z. Chem. 5, 323 (1869).

[2] D. Krull. Kali 17, H. 6, 67 (1933).

[3] A. E. Hill, J. Am. Chem. Soc., 59, 2242 (1937).

[4] D.N.Shoykhet and E.I.Lukyanova. Collected Researches of the Workers of the State Inst. of Applied Chem., 34 (1940).

[5] W.J.Lightfoot and C.F.Prutton. J. Am. Chem. Soc. 69, No. 9, 2098 (1947).

[6] G.H.Assarsson, J. Am. Chem. Soc. 72, No. 4 (1950).

[7] E.P.Dergunov and A.G.Bergman. Proc. Acad. Sci. USSR, 75, No. 6, 815 (1950).

[8] J.H.van't Hoff. Ocean Salt Deposits (1936).

[9] V.N.Sveshnikova. Bull.Section Phys. Chem. Anal. 17, 345 (1949).

[10] N.S.Kurnakov. Magnesia Lakes of the Perekop Group. Bull. Acad. Sci., Petrograd, 137 (1917).

[11] G.G.Yrazov. Investigation of the Lakes of S. Russia. (1919).

[12] Yu.V.Morachevsky. Notes on the Geochemistry of the Higher Kama Salt Deposits. (1939).

BLANK
PAGE

CATALYTIC OXIDATION OF ETHYLENE ON MAGNESIUM CHROMITE

L. Ya. Margolis and O. M. Todes

In a previous work [1] we have studied the kinetics of the oxidation of isooctane and ethylene in stream-form at catalysts belonging to the structural type of spinels (chromites, aluminates, etc.). The study under dynamic conditions of the determining stage of the oxidation process at various catalysts in presence of various additives does not seem possible. In this paper we give the results of a study of the oxidation of ethylene in a vacuum system under static conditions at low pressure (0.1-2 mm Hg). As under streaming conditions at catalysts of the type $Me^{II}M_2^{III}O_4$, the reaction goes to completion, i.e., to carbon dioxide and water.

EXPERIMENTAL

1. Gases

Ethylene was prepared by the dehydration of ethyl alcohol at active aluminum oxide and was purified by continual freezing out and filtration through active charcoal. Oxygen was prepared by the decomposition of potassium permanganate that had been recrystallized twice; impurities were removed by freezing out.

2. Catalyst

For the investigation a magnesium-chrome catalyst, consisting of a mixture of magnesium chromite with excess magnesium oxide, was chosen. As an additive, sodium silicate was used. The specific surface of the magnesium-chrome catalyst was measured by adsorption of nitrogen at 183°; it was 70 m^2/g. Elovich and coworkers have studied the adsorption isotherms of propene on these catalysts at -23 and -63° over a wide range of pressures (10^{-4} mm Hg-700 mm Hg) by weighing on a McBean quartz balance. The heterogeneity of the surface was analyzed by Roginsky's method, and it was shown that the magnesium-chrome catalyst has a very heterogeneous surface, with a wide variety of sites with respect to molecular heat of sorption. On introducing the additives into the catalyst, the specific surface did not change appreciably.

3. Arrangement of Apparatus and Procedure

The study of the oxidation of ethylene by oxygen was carried out in a static system, represented in Figure 1. From the gas-holder flasks 2, 3, and 4, gas proceeds to the manifold 1 and is admitted through the taps 15 and 16 to the reactor 10. The latter is contained in an electric furnace 11, the p.d. across which is regulated by means of a variable resistance, which is switched in across a stabilizer. The temperature is measured at the wall of the reactor by means of a copper-constantan thermocouple and a potentiometer. The variation in temperature did not usually exceed ±2°. In a number of cases, in order to obtain more accurate measurements, baths containing constant-boiling liquids (ethyl alcohol 78°, toluene 110°, aniline 184°) were used. The upper joint of the reactor was surrounded by solid carbon dioxide to protect the catalyst from the vapor of the grease. Water formed in the reaction was frozen out in the trap 12, which was immersed in a Dewar vessel containing solid carbon dioxide. The reaction was followed by the fall in pressure in the McLeod gage 7, joined to the fore-vacuum flask 9.

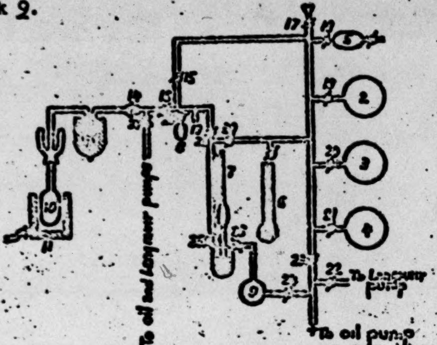


Figure 1. Diagram of apparatus: 2,3,4) gas collectors; 5) calibrated volume; 6) manometer; 7) McLeod gage; 8) absorber containing alkali; 9) fore-vacuum flask; 10) reactor; 11) electric furnace; 12) trap; 13) side-tube for gas analysis; 14) joint; 15-31) taps.

Also, the amount of carbon dioxide formed was measured by absorption by solid caustic alkali in the absorber 8 and by freezing it out in the side tube 13. The procedure was as follows: a weighed amount of catalyst was placed in the reactor (0.02-0.2 g magnesium chromite), protected with the aid of solid carbon dioxide from the vapor of grease, and activated at 450° for 2 hours. The temperature was then brought to that required in the experiment and maintained at that level for one hour. Under identical conditions in absence of catalyst the transfer coefficients of the gases used were determined at various temperatures. Pure ethylene, pure oxygen, or a stoichiometric mixture of these gases was transferred from a definite volume into the reactor, and the kinetics of the oxidation reaction were followed by the change in pressure; the water formed in the reaction was frozen out in the trap, which was surrounded by solid carbon dioxide. At definite intervals the gas mixture was analyzed for its content of carbon dioxide, ethylene, and oxygen.

4. Oxidation of a Stoichiometric Mixture of Ethylene and Oxygen

In Figures 2, 3, and 4, kinetic curves are given for the oxidation of a stoichiometric mixture of ethylene and oxygen. Expressed in coordinates of pressure change (mm Hg) and time t (min.), the curve at first rises steeply and then saturation sets in.

Under static conditions at low pressure, with repeated reaction the oxidation process became slower until it reached a constant condition, which did not change in further experiments. In the oxidation of a mixture of ethylene and air under dynamic conditions, the activity of the magnesium-chrome catalyst remained unaltered for a long period. The lowering of the activity of the catalyst under static conditions may be explained by a reversible or irreversible poisoning of the surface. The filling of the active sites by one of the components of the reaction can lead to a reduction in the rate of reaction. Simultaneously with the catalytic reaction, chemisorption [2] may proceed, and this, according to a number of investigators, is a complex process, leading on the one hand to the activation of the molecules of the reacting substances at the surface, and on the other hand to the non-participation of molecules that are firmly bound to the surface in the reaction; in this latter case, chemisorption becomes a blind alley for the reaction. From this point of view, a detailed analysis of the balance of the reaction makes it possible to separate the processes of chemisorption and of reaction. It is shown in Table 1 that as reaction is repeated for a stoichiometric mixture the proportion of oxidized ethylene constantly falls and after 5 experiments amounts to only 18%, whereas the proportion of sorbed ethylene on the surface of the catalyst rises from experiment to experiment and attains 60%. The fall in the overall rate (see Figures 2 and 3) and the attainment of a so-called "stationary" state are deceptive, for under these conditions ethylene scarcely undergoes oxidation and only blocks the surface of the catalyst. Simultaneously with the sorption of ethylene, sorption of oxygen, which does not react with the ethylene, occurs. At the same time it should be noted that the proportion of unused ethylene (residue) remains constant, i.e., the surface is not saturated with sorbed hydrocarbon, whereas the proportion of unused oxygen increases from experiment to experiment and attains 20%. In other words, either the activation energy for the sorption of ethylene is considerably greater than that for oxygen so that the process is determined by the sorption of ethylene, or they are sorbed at different sites, and the proportion of adsorption sites for oxygen is considerably less than for ethylene.

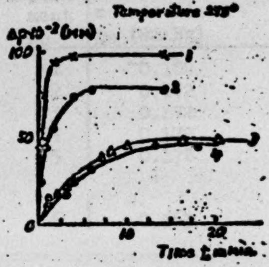


Fig. 2. Dependence of the reaction rate (pressure change) for the oxidation of ethylene at 275° on time; 1, 2, 3 and 4 indicate successive experiments.

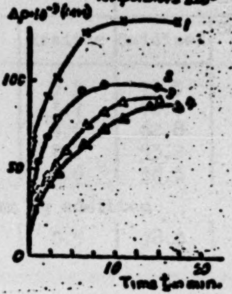


Fig. 3. Dependence of the reaction rate for the oxidation of ethylene at 320° on time; 1, 2, 3, 4 as before.

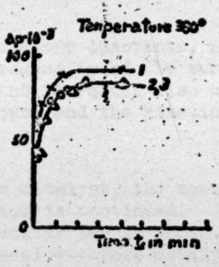


Fig. 4. Dependence of the reaction rate for the oxidation of ethylene at 380° on the time.

It is possible that in addition to sorption the process of the dissolution of oxygen in the catalyst may occur. The "poisoned surface" may be regenerated by reaction with oxygen in the gas phase (Experiment 6, Table 1); the surface ethylene is burned out, and the activity of the catalyst is practically fully regained.

When the reaction is carried out in a gas stream with excess of oxygen, regeneration of the catalyst surface by oxygen is occurring constantly, and therefore the activity of the catalyst does not alter over a long period. Change

TABLE 1

Reaction Balance for the Oxidation of a Stoichiometric Mixture of Ethylene and Oxyge

Experiment No.	Initial pressure of the stoichiometric mixture p_o (mm Hg)	Ethylene (%)			Oxygen (%)		
		Oxidized	Sorbed on surface	Residue	Oxidized	Sorbed on surface	Residue
1	0.182	79.5	14.3	5.5	79.5	14.5	5.5
2	0.172	70.0	26.3	3.7	70.0	20.8	8.2
3	0.172	62.8	32.6	4.6	62.8	23.8	13.4
4	0.172	53.2	42.2	2.1	53.2	27.3	19.5
5	0.172	18.6	60.6	1.6	18.6	51.3	20.1
		Oxygen at 99 mm Hg admitted					
6	0.163	78,0	21.0	0.5	78.0	20.5	0.5

in the activity of the catalyst would no doubt occur in catalytic oxidation reactions with less than the stoichiometric proportion of oxygen. Analogous changes in the surface have been observed by Elovich and coworkers in a study of the oxidation of CO at MnO_2 [2].

The process is expressed by the following kinetic equation:

$$\frac{dq}{dt} = ac^{-\alpha q}(q_o - q), \qquad (1)$$

where q is the amount of reacting substance, α and a are constants, and t is the time. The coefficient α is a measure of the heterogeneity of the surface with respect to energy. As the process is continued, and therefore also chemisorption, the surface becomes leveled out and more homogeneous, and the kinetic equation goes over into a unimolecular one:

$$w = k(q_o - q). \qquad (2)$$

In the oxidation of ethylene at a magnesium-chrome catalyst, the same kinetic law is observed, and the surface changes as the reaction is continued. In Figure 5, the transition of the reaction over to the unimolecular law is shown. On introducing an additive (sodium silicate) into the magnesium-chrome catalyst, the equation for the oxidation reaction of ethylene, both under dynamic conditions at atmospheric pressure and under static conditions at low pressure, is not affected.

In Figure 6, results are shown for the oxidation of ethylene at a catalyst containing various amounts of additive. If the reaction rate equation is as follows

$$w = w_o e^{-\alpha \Delta p}, \qquad (3)$$

where w_o is the initial rate, α is a coefficient, and Δp is the change in pressure resulting from reaction in mm, then

$$\frac{1}{2,3}\alpha \Delta p = \log \alpha w_o + \log \left(t + \frac{1}{\alpha w_o}\right)$$

When this equation is written for two experimental points and one is divided by the other [4] we obtain

$$\frac{\log(1 + \alpha w_o t_1)}{\log(1 + \alpha w_o t_2)} = \frac{\Delta p_1}{\Delta p_2}.$$

By choosing the two points so that

$$\frac{\Delta p_1}{\Delta p_2} = 2$$

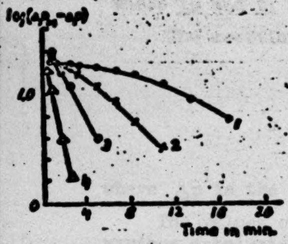


Fig. 5. Kinetic curves for the oxidation of ethylene: 1,2,3,and 4 indicate successive experiments

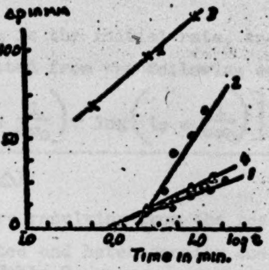


Fig. 6. Dependence of the rate of oxidation reaction of a stoichiometric mixture of ethylene and oxygen at various catalysts at 320° on the log of time: 1) magnesium-chrome catalyst, 2) magnesium-chrome + 1% sodium silicate, 3) magnesium-chrome + 2% sodium silicate, 4) magnesium-chrome + 3% sodium silicate

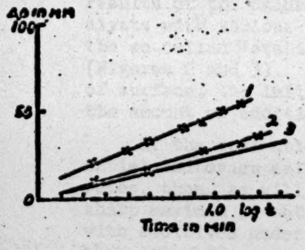


Fig. 7. Dependence of the reaction rate of the oxidation of ethylene at 300° for different catalysts at stationary activity on the log of the time: 1) magnesium-chrome catalyst, 2) magnesium-chrome + 1% sodium silicate, 3) magnesium-chrome + 2% sodium silicate, 4) magnesium-chrome + 3% sodium silicate

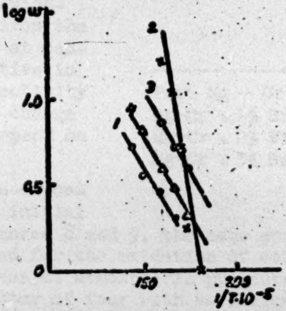


Fig. 8. Dependence of the log of the initial reaction rate of oxidation at a surface in the "stationary" state on 1/T for different catalysts: 1) magnesium-chrome catalyst, 2) magnesium-chrome + 1% sodium silicate, 3) magnesium-chrome + 2% sodium silicate, 4) magnesium-chrome + 3% sodium silicate

we obtain

$$\alpha w_0 = \frac{t_2 - 2t_1}{t_1^2}$$

where t_2 and t_1 are the times, w_0 is the initial rate, and α is a coefficient.

The coefficient α is calculated from the following equation

$$\alpha = \frac{2.3\left[\log\left(t_1 + \frac{1}{\alpha w_0}\right) - \log\left(t_2 + \frac{1}{\alpha w_0}\right)\right]}{\Delta p},$$

where Δp is the change in pressure resulting from the reaction.

The values of the initial rates and heterogeneity coefficients α for the various catalysts are given in Table 2.

As will be seen from the table, the initial rate, which corresponds to maximum activity, varies by a factor of 100. On introducing the additive, the coefficient α at first falls very sharply, and then rises slowly It is interesting to note that variation in the content of additive evidently leads to variation in the extent to which chemisorption participates in the reaction of the oxidation of ethylene. In Figure 7 are given the results of the oxidation of ethylene at catalysts with various contents of additive in the so-called "stationary state" of activity (Figures 2 and 3). Even with such a change of surface, the initial rate and α depend on the amount of additive.

TABLE 2

Initial Reaction Rates for the Oxidation of Ethylene and Heterogeneity Coefficients for Various Catalysts

Catalyst	Initial rate (mm/min)	Heterogeneity coefficient α(mm^{-1})
Pure Mg – Cr	9.7	0.120
Mg–Cr + 1% SiO_2	9.3	0.010
Mg–Cr + 2% SiO_2	1058.0	0.050
Mg–Cr + 3% SiO_2	8.9	0.075

If the activation energy and pre-exponential factor are calculated from the initial rates, then, as will be seen from Figures 8 and 9, the same sort of curve with a sharp maximum is obtained as was found for the oxidation of ethylene at catalysts with additives under dynamic conditions at atmospheric pressure The value of the activation energy varies by a factor of four with variation in the content of additive in the catalyst.

SUMMARY

1. A study has been made of the oxidation reaction of ethylene at a magnesium-chrome catalyst with an addition of sodium silicate under static conditions under a pressure of up to 2 mm Hg.

2. It is shown that the activity of the catalyst varies owing to the simultaneous occurrence of two processes – oxidation and sorption of a component.

3. The activity of the catalyst is restored by treatment of the surface with oxygen.

4 Under dynamic conditions with a great excess of oxygen, the surface is continuously regenerated, and the activity of the catalyst remains unaltered over a long period.

5. In the oxidation of ethylene under static conditions at catalysts with additives, the characteristic peculiarities of the modification phenomenon, which we observed in our earlier dynamic experiments, were observed again.

Institute of Physical
Chemistry of the USSR
Academy of Sciences

Received July 18,1950

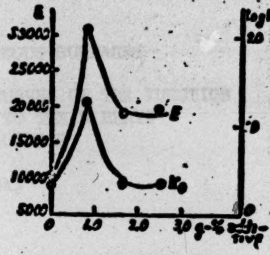


Fig. 9. Dependence of the activation energy and the logarithm of the pre-exponential factor on the content of additive for the oxidation of ethylene at catalysts in the "stationary state" of activity.

LITERATURE CITED

[1] L. Ya. Margolis and O. M. Todes. Bull. Acad. Sci. USSR, Div. Chem. Sci., 5, 443 (1947); Proc. Acad. Sci. USSR, 8, 3, 421 (1947).

[2] S. Yu. Elovich. J. Phys. Chem., 9, 10 (1940); S. Z. Roginsky and S. Yu. Elovich. Bull. State Nitrogen Inst., 7 (1938); B. P. Bruns. J. Phys. Chem., 21, 1011 (1947).

BLANK
PAGE

THE THEORY OF CHROMATOGRAPHY ON HETEROGENEOUS SURFACES

COMMUNICATION 1. DETERMINATION FROM DESORPTION CURVES OF THE FUNCTION EXPRESSING THE DISTRIBUTION WITH RESPECT TO THEIR HEATS OF ADSORPTION OF SITES ON A SOLID SURFACE

S. Z. Roginsky and M. I. Yanovsky

Recent work has shown clearly that it is impossible to base the theory of the adsorption of individual substances and mixtures on concepts that relate to a homogeneous surface. The development of the statistical theory of adsorption phenomena, which takes into account the presence on a solid surface of sites with widely varying adsorption and kinetic coefficients, has enabled these difficulties to be largely eliminated. For low and medium site-occupation, the theory of heterogeneous surfaces is in good agreement with experimental results [1].

The theory of chromatographic separation processes, which were first discovered by Tsvet [2], can be constructed only with a knowledge of the adsorption statistics; hence, in working out the theoretical basis of separation by adsorption it is necessary to take the results of statistical theory into account. This is particularly important in the region of low site-occupation.

As statistical analysis of the adsorption equilibria of individual substances shows, the character of the isotherms is determined by the so-called distribution functions $\rho(Q)$, expressing distribution with respect to heats of adsorption of sites on the surface. For the adsorption of mixtures, the character of the adsorption equilibrium at a heterogeneous surface is determined by the form of the functional relationship between the heats of adsorption of the components of the mixture at the same sites [3], as well as by $\rho(Q)$. In the present work, the possibility of applying relatively simple chromatographic measurements to the determination of the distribution function $\rho(Q)$ has been investigated.

According to statistical theory, the process occurring at an active surface is the overall result of the summation of a number of independent processes occurring on different sites. In many cases, summation may be replaced by integration. If, for example, any property F(x) of the surface S depends on the variable x, then, for a surface that is not homogeneous with respect to x, the value of the property F(x) is expressed by the following integral [4]:

$$F(x) = \int_{x_1}^{x_2} f(x)\,\rho(x)\cdot dx. \qquad (1)$$

Here $\rho(x)$ is the distribution function for the surface S with respect to the variable x, or in other words, $\rho(x)$ is the "statistical weight" of sites having a given value of x, i.e.,

$$\rho(x) = \frac{dS(x)}{dx},$$

$\underline{f}(x)$ gives the dependence of $\underline{F}$, the property studied, on $\underline{x}$ for a homogeneous surface,

Knowing $\rho(x)$, $F(x)$ can be calculated for a heterogeneous surface, and, on the other hand, knowing the law expressed by $F(x)$, the distribution function $\rho(x)$ may be found.

With regard to the application of this to adsorption equilibria, an interesting integral property of a heterogeneous surface is the amount of adsorbed substance as a function of the concentration $\Phi(c)$. The heat of adsorption $\underline{Q}$ on separate sites on the surface is chosen as variable. Replacing $\underline{x}$ by $\underline{Q}$ in the integral of Equation 1, we obtain:

$$\Phi(c) = \int_{Q_1}^{Q_2} \underline{f}(c)\rho(Q)dQ. \tag{2}$$

Here $\underline{f}(c)$ represents the isotherm for adsorption on a homogeneous surface; it is in its turn a function of the heat of adsorption $\underline{Q}$. $\rho(Q)$ is the distribution function of surface sites with respect to heats of adsorption $\underline{Q}$. $Q_2 - Q_1$ is the interval over which the heats of adsorption vary. The strict solution of the integral of Equation 2 generally presents considerable mathematical difficulties [5], but, as one of us has shown [1], when the interval over which the heats of adsorption vary is sufficiently wide, the solution of the integral of Equation 2 may be often replaced with sufficient accuracy by the solution of the simpler integral:

$$\Phi(c) \approx \int_{Q_n = RT\ln\frac{b_0}{c}}^{Q_{max}} \rho(Q)dQ \tag{3}$$

Here b_0 is a constant in the equation for the desorption factor in Langmuir's isotherm.

$$b = b_0 e^{-Q/RT}.$$

From Equation 3 a simple method can be found for determining the distribution function $\rho(Q)$ from a given adsorption isotherm $\Phi(c)$ for a heterogeneous surface. For this purpose it is sufficient to integrate Equation 3 for the lower limit:

$$\rho(Q) = \frac{1}{RT}\frac{d\Phi(c)}{d\ln c}. \tag{4}$$

Equation 4 permits a direct graphical treatment of the experimental isotherm $\Phi(c)$ without previously determining its analytical expression. For this purpose it is sufficient to plot the experimental points in the co-ordinates $\Phi(c)$ - ln $\underline{c}$ and to perform graphical differentiation. Concrete examples of the analysis of experimental results on adsorption equilibria with the aid of Equation 4 are given in a special monograph [1].

In chromatographic practice, the determination of adsorption isotherms in the region of low saturation may present considerable difficulties. In such cases, Equation 4 cannot be used for determining $\rho(Q)$. However, owing to a definite resemblance of Equation 4 to the generally known fundamental equation of chromatography [6] the function $\rho(Q)$ can be readily determined from the desorption curves. The essence of the proposed method lies in the following. The fundamental equation of chromatography [6] gives the following simple relationship between the main parameters of the chromatographic process:

$$\frac{V}{x} = M\frac{d\Phi(c)}{dc} = M\Phi'(c) \qquad (5)$$

or

$$\Phi'(c) = \frac{1}{M} \cdot \frac{V}{x} . \qquad (5a)$$

Here, V is the volume of the solution that has passed; x is the distance from the beginning of the column, measured in the direction of flow; $c = c(x,V)$, the variable concentration of the substance being sorbed in the column; $\Phi(c)$ is the value of the adsorption isotherm at concentration c; M is the weight of a linear cm of charge, when the column is of constant cross-section.

As is well known, Equation 5 is applicable both to adsorption and to desorption of the substance. When a slow stream (concentration of sorbate – c) passes through a layer of carefully ground adsorbent, a sharp "front" is formed. To the left of the front, the sorbent is saturated up to the value $\Phi(c_0)$, determined by the initial concentration c_0. To the right of the front, the sorbent is completely free from sorbate. Thus, for adsorption from a stream, Equation 5 leads to Shilov's model [7] with an infinitely thin "working layer", which, in absence of "wall" effects and "protuberances" [8], lies perpendicular to the direction of flow. Strictly speaking, Equation 5 is correct only when adsorption equilibrium is established instantaneously in the layer and when longitudinal diffusion can be neglected in comparison with the transfer of substance by the moving stream. Of considerably greater interest is the use of Equation 5 for the dynamic desorption of a substance from a layer by a non-sorbable gaseous or liquid carrier. As already shown [9], in this case the fore-front of the sorbed substance moves forward through the layer without changing its sharpness, and the hind-front is gradually drawn out, its form and magnitude being determined by the form of the adsorption isotherm.

Combining Equations 4 and 5, we may greatly simplify the problem of determining $\rho(Q)$. For this purpose we shall write Equation 4 in the following form:

$$\rho(Q) = \frac{d\,\Phi(c)}{RT\,d\ln c} = \frac{c}{RT}\,\frac{d\Phi(c)}{dc} = \frac{c}{RT}\,\Phi'(c).$$

Substituting in Equation 4 the value of $\Phi'(c)$ from Equation 5a, we obtain:

$$\rho(Q) = \frac{cV}{MxRT} . \qquad (6)$$

By using Equation 6, the problem of determining $\rho(Q)$ amounts only to the standard chromatographic measurement of the desorption curve $\underline{c} = \underline{c}(x,V)$ giving the relation between the concentration $\underline{c}$ of the substance in the liquid or gaseous carrier after passing through a sorbent layer of length $\underline{x}$ and the amount $\underline{V}$ of pure carrier entering the column during this time.

In Fig. 1, a typical desorption curve is represented diagrammatically. This curve will be described by Equation 5 if, in addition to the conditions indicated above, the following conditions are observed:

1) dynamic desorption is carried out by a non-sorbing carrier;
2) the adsorption isotherm is convex to the axis of ordinates and has no points of inflection.

In its first part, the desorption curve ABCD is characterized by the presence of the horizontal section AB at a distance of $\underline{c} = \underline{c}_0$ from the V-axis, where c_0 is the initial concentration of the adsorbate at which the layer becomes saturated. Beyond the horizontal section there is at first a fairly sharp fall in the effluent concentration, but later the rate of fall dc/dV diminishes considerably, particularly in regions of low concentration. It will be seen from Fig. 1 that the distribution function $\rho(Q)$, defined by Equation 6, is proportional to the area OGCE, which is shaded in the figure, and inversely proportional to the product MxRT:

$$\rho(Q) = \frac{\text{area OGCE}}{\text{MxRT}} \qquad (6a)$$

The falling portion of the desorption curve yields a simple method for constructing the graph of the function $\rho(Q)$. For this purpose, the value of $RT \ln c$ is taken as abscissa (it is proportional to the heat of adsorption Q), and the value of $\underline{Vc}$, proportional to the distribution function $\rho(Q)$, is taken as ordinate (Fig. 2).

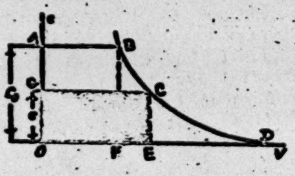


Fig.1. Determination of the distribution function with respect to heats of adsorption for sites on the surface

$$\rho(Q) = \frac{\text{area OGCE}}{\text{MxRT}}$$

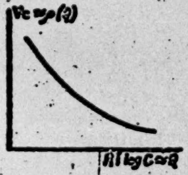


Fig. 2. Construction of the graph for $\rho(Q)$ in accordance with the desorption curve $\underline{c} = \underline{c}(V)$.

Thus, when we have the desorption curve $\underline{c} = \underline{c}(V)$, we may construct the graph $\rho = \rho(Q)$ without having recourse to adsorption measurements.

If the equation of the desorption curve $\underline{c} = \underline{c}(V)$ is given in explicit form, then, in accordance with Equation 6, there is no difficulty in determining $\rho(Q)$, and, on the other hand, if the function $\rho(Q)$ is known, then it is easy to find the desorption curve $\underline{c} = \underline{c}(V)$. Let us examine, for example, the frequently occurring case of distribution in accordance with a power law:

$$\rho = HQ^n. \tag{7}$$

Substituting $\rho(Q)$ in quation 6 by its value from Equation 7, and replacing Q by RT ln $\frac{b_o}{c}$, we obtain, after elementary rearrangement:

$$\frac{c}{\left(\ln \frac{b_o}{c}\right)^n} = \frac{HMx(RT)^{1+n}}{V} \tag{8}$$

Equation 8 is the general equation of desorption curves for distributions according to a power law. For exponential distribution

$$\rho = He^{-\alpha Q}, \tag{9}$$

where α is the coefficient of non-uniformity, and we have

$$\alpha = (nRT)^{-1}$$

and

$$H = \frac{ab_o^{1/n}}{n \cdot RT},$$

In an analogous manner we obtain the following equation for the desorption curve:

$$c = \frac{(HMxRT)^{1/1+\alpha RT} \cdot b_o^{\alpha/RT(1+\alpha RT)}}{V^{1/1-\alpha RT}}. \tag{10}$$

It is interesting to note that when α and $\underline{n}$ tend to zero, both the exponential and the power distributions go over into a uniform distribution:

$$\rho = H. \tag{11}$$

for which the equation of the desorption curve takes up the following simple hyperbolic form:

$$c = \frac{HMxRT}{V}. \tag{12}$$

It should be emphasized that over short ranges the exponential distribution is often indistinguishable from the power distribution, and hence conclusions concerning the character of the distribution made from the desorption curve may be made only when the range of measured concentrations is sufficiently wide.

SUMMARY

1. The effect of energetic inhomogeneity of the surface on the character of the dynamic desorption curves in chromatographic analysis has been analyzed.

2. The relation between the form of desorption curves $\underline{c} = \underline{c}(V)$ and the form of the function expressing the distribution with respect to their heats of adsorption of sites on the surface $\rho(Q)$ has been obtained.

3. A method is given for the construction of $\rho(Q)$ from desorption curves without having recourse to special adsorption measurements.

4. The equations of desorption curves for the fundamental forms of distribution are obtained.

5. The limits and conditions of applicability of the proposed method are pointed out.

LITERATURE CITED

[1] S. Z. Roginsky. Adsorption and Catalysis at Heterogeneous Surfaces. 1948.

[2] M. S. Tsvet. Chromatographic Adsorption Analysis (Selected Papers). U.S.S.R. Acad. Sci. Press, 1946.

[3] S. Z. Roginsky and O. M. Todes. Acta Phys. Chim., 20, 507, 695 (1945).

[4] V. I. Levin, Prog. Chem., 17, 174 (1948)

[5] O. M. Todes, A. K. Bondareva. J. Appl. Chem., 1948; V. I. Levich and M. I. Temkin. J. Phys. Chem., 20, 12 (1946).

[6] De Vault, J. Am. Chem. Soc. 65, 532 (1943).

[7] M. M. Dubinin. Physicochemical Basis of Sorption Technology 1932.

[8] L. V. Radushkevich. Proc. Acad. Sci. U.S.S.R., 57, 471 (1947)

[9] S. Z. Roginsky and M. I. Yanovsky Proc. Acad. Sci. U.S.S.R., 65, 6, 879 (1949)

Institute of Physical Chemistry
of the U.S.S.R. Academy of Sciences

Received August 18, 1949

THE THEORY OF CHROMATOGRAPHY ON HETEROGENEOUS SURFACES

COMMUNICATION 3. DYNAMICS OF THE ADSORPTION OF MIXTURES ON HETEROGENEOUS SURFACES

S. Z. Roginsky and M. I. Yanovsky

The dynamics of the adsorption of mixtures for medium degrees of saturation have been studied in a number of investigations [1,2,3]. The theoretical concepts of this field have recently been applied to chromatographic adsorption analysis, which was discovered by Tsvet [4]. At the basis of the so-called " chromatographic frontal analysis" lies the application of the Shilov-Dubinin [6] "parallel transfer" principle to the case of the adsorption of mixtures that conform to Langmuir's equation, which is typical for energetically homogeneous surfaces.

The assumption of the energetic homogeneity of the surface of the adsorbent does not generally lead to great complications for medium degrees of saturation, inasmuch as the Langmuir equation is a sufficiently good interpolation formula in this region. The picture changes sharply when we go over to a low total saturation, for it is then impossible to have only medium saturation θ and medium desorption coefficients b for all the surfaces of the adsorbent.

The recent development of the statistical theory of adsorption [7] and the extension of the conclusions from this theory to the adsorption of mixtures [8] permits the dynamics of the adsorption of mixtures at low saturation to be analyzed in greater detail.

In the present work, which is based on the conclusion of statistical theory [7,8], an attempt is made to expose the typical peculiarities of the dynamics of the adsorption of mixtures at a heterogeneous surface.

Adsorption Equilibrium

In accordance with statistical theory, the character of the adsorption equilibrium of a mixture of two substances at a heterogeneous surface is determined by the form of the functional relation between the heats of adsorption Q_1 and Q_2 of the components of the mixture on one type of site:

$$Q_2 = \varphi(Q_1). \qquad (1)$$

As we cannot go into detail concerning the dependence of this functional relationship on the nature of the adsorption forces, we will point out only the probability of the existence of three fundamental cases: a symbathic relationship, an antisymbathic relationship, and absence of any relationship between the heats of adsorption of the components.

From the point of view of the practical chromatographic separation of liquid organic mixtures and gases, the case of a symbathic relationship between the heats of adsorption is the most interesting. Such a relationship is to be expected, in particular, for all cases of adsorption that result mainly from the operation of dispersion forces, e.g., in the adsorption of mixtures of aliphatic hydrocarbons, of mixtures of inert gases, etc , when chromatographic separation, owing to the closeness of the adsorption coefficients, meets with particularly great difficulty. The simplest example of the symbathic change of Q_1 and Q_2 is the case of direct proportionality between the heats of adsorption:

$$Q_2 = \beta Q_1. \tag{2}$$

In the present work, we are confining ourselves to the analysis of this one simple case, which is often met in practice.

In Fig. 1 is shown the graph used in statistical theory [8] for analyzing the equilibrium of a mixture of two substances. Along the axis of abscissas, the heat of adsorption of one of the components, e.g., Q_1, is given, and along the other axis – the following quantities:

$\rho(Q)$, the function expressing the distribution with respect to their heats of adsorption Q_1 of sites on the surface. This quantity is determined by the fraction of the surface occupied by sites having heats of adsorption lying within the limits Q_1 to $Q_1 + dQ_1$.

b_1, the desorption coefficient of the first substance.

b_2, the desorption coefficient of the second substance.

The relations between the desorption coefficients and the heat of adsorption are given by the following equations:

$$b_1 = b_{01}e^{-Q/RT} \tag{3}$$

and

$$b_2 = b_{02}e^{-Q/RT} \tag{3a}$$

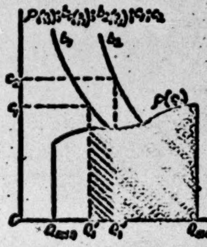


Fig. 1. Initial graph for the analysis of the adsorption equilibria of a mixture of two substances.

The desorption coefficients b_1 and b_2 are numerically equal to the concentrations c_1 and c_2 at which, in absence of other substances, half the surface is occupied ($\theta = 0.5$). Hence, along the ordinate axis in Fig. 1, we may give also values of the concentrations c_1 and c_2. It follows from the above that from the intersections of the $b_1(Q_1)$ and $b_2(Q_1)$ with the straight lines c_1 = const. and c_2 = const. we may determine the heats of adsorption Q'_1 and Q'_2 of the corresponding groups of sites on the surface of the adsorbent, half of which is filled by sorbate. In view of the steep exponential relationship between the saturation θ and the heat of adsorption Q, it may be assumed that on the distribution graph $\rho(Q)$, to the left of Q_1 ($b_1 > c_1$) the surface is practically free from the first substance ($\theta_1 \approx 0$), and to the right of Q_1 ($b_1 < c_1$) it is fully occupied ($\theta \approx 1$). Analogous considerations apply for substance 2:

to the left of Q''_1 ($b_2 > c_2$) and $\theta_2 \approx 0$,

to the right of Q''_1 ($b_2 < c_2$) and $\theta_2 \approx 1$.

When adsorption from a mixture is characterized by a fight for the surface, the ratio of the fractions of the surface occupied by the components will be determined by the ratios c_1/b_1 and c_2/b_2:

$$\Delta = \frac{\theta_2}{\theta_1} = \frac{c_2}{c_1}\,\frac{b_1}{b_2} = \frac{c_2}{c_1}\,\frac{b_{01}}{b_{02}}\, e^{\frac{(\beta-1)Q_1}{RT}} \qquad (4)$$

From Equation 4 it will be seen that there is a possibility of a considerable preponderance of one of the gases on certain sites of the surface and even over the whole surface.

This is shown in Fig. 2, in which there are plotted as abscissas not only b_1, b_2, c_1, c_2, and $\rho(Q)$, but also the ratio b_2/b_1 of the desorption coefficients and the concentration ratio c_2/c_1. The abscissa Q_1^* of the intersection of the straight line c_2/c_1 = const. with the curve $b_2/b_1(Q_1)$ is the limit to the left of which the surface is practically completely occupied by substance 1 and to the right of which – by substance 2. Analytically, Q_1^* is found from the equation:

$$Q_1^* = \frac{RT}{\beta - 1} \ln \frac{c_1}{c_2}\,\frac{b_{01}}{b_{02}}. \qquad (5)$$

The ordinate c_1^* of the point of intersection of the straight line Q_1^* = const. with the curve $b_1(Q_1)$ permits calculation of the extent of the adsorption of the components on the basis of the adsorption isotherms of the pure substances:

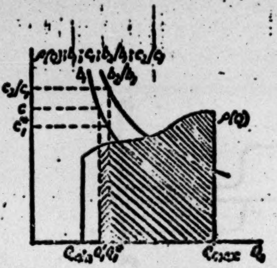


Fig. 2. Determination of the distribution of two substances when the heats of adsorption are symbathically related

$$\underline{f}_1(c_1c_2) = \int_{Q_1'}^{Q_1^*} \rho(Q)dQ =$$

$$= \int_{Q_1'}^{Q_{max}} \rho(Q)dQ_1 - \int_{Q^*}^{Q_{max}} \rho(Q)dQ = \underline{f}_1(c_1) - \underline{f}_1(c_1^*). \qquad (6)$$

$$\underline{f}_2(c_1c_2) = \int_{Q_1^*}^{Q_{max}} \rho(Q)dQ = \underline{f}_1(c_1^*). \qquad (7)$$

The value of c_1^* may be found, also analytically, from the equation:

$$c_1^* = b_{01}e^{-Q^*/RT} = b_{01}(c_2/c_1\cdot b_{01}/b_{02})^{1/\beta-1} \qquad (8)$$

Dynamics of Adsorption

We will examine the movement of the mixture through a layer of adsorbent, assuming instantaneous establishment of equilibrium at each point of the layer and neglecting the effect of diffusion along the direction of the stream in comparison with the velocity of the stream. This leads to the diagram shown in Fig. 3 [1,2,3].

Two sorption waves move through the layer. The first substance, which is sorbed less readily than the second, moves with the greater velocity. The movement of the adsorption wave of the more readily sorbing substance 2 is accompanied by partial desorption of the less readily sorbing substance 1, and, for this reason, the concentration c'_1 of this substance in the first wave is higher than the influx concentration c_1^0. The distribution of adsorbed substances corresponding to Fig. 3 is shown diagrammatically in Fig. 4. Separate sections of the distribution curve and also the concentration c'_1 of substance 1 in the first sorption wave can be calculated for the case of symbathically related heats of adsorption in the following manner. We start from the adsorption isotherms for the components of the mixture (Equations 6 and 7).

We will suppose that a certain volume V_0 of gaseous carrier containing the sorbates in concentration c_1 and c_2^0 is passed through the charge. The width x_2 of the zone in which both substances are adsorbed is determined by the following obvious relationship, which is valid so long as the amount of substance contained in the space not occupied by adsorbent is neglected:

$$\frac{V_0}{x_2} = \frac{f_2\,(c_1^0,\ c_2^0)}{c_2^0} \tag{9}$$

⑥

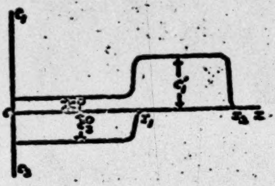


Fig.3. Distribution of concentrations along the length of the layer (adsorption dynamics of a mixture of two substances for $c_2 \ll c_1$)

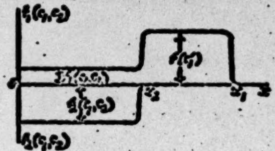


Fig.4. Distribution of the adsorbed substances over the length of the layer for $c_2 \ll c_1$

Substituting $f_2'(c_1,c_2)$ by its value from Equation 7, we obtain

$$x_2 = \frac{V_0 c_2^0}{\underline{f}_1(c_1^*)}\,. \tag{9a}$$

The quantity m_{1x_2} of substance 1 sorbed in the layer x_2 is found in the following manner:

$$m_{1x_2} = \underline{f}_1(c_1^0,\ c_2^0) \tag{9b}$$

We substitute the value of $\underline{f}_1(c_1^0,c_2^0)$ from Equation 6 and the value of x_2 from equation 9a in equation 9b:

$$m_{1x_2} = \frac{V_0 c_2^0}{\underline{f}_1(c_1^*)}\,[\underline{f}_1(c_1^0) - \underline{f}_1(c_1^*)]\,. \tag{9c}$$

The quantity $m_{1x_1x_2}$ of substance 1 adsorbed in the first sorption wave is determined by taking the difference between the total amount m_1 entering the layer in volume V_0 and the amount m_{1x_2} adsorbed on the section x_2:

$$m_{1x_1x_2} = m_1 - m_{1x_2} = V_0 c_1^0 - \frac{V_0 c_2^0}{\underline{f}_1(c_1^*)}\cdot[\underline{f}_1(c_1^0) - \underline{f}(c_1^*)]. \tag{9d}$$

Hence we can define the width of the zone $x_{1,2}$ in which only substance 1 is adsorbed without admixture of substance 2:

$$x_{1,2} = \frac{m_1 x_1,\ x_2}{f_1(c_1^1)} = \frac{V_0 c_1^0}{f_1(c_1^1)} - \frac{V_0 \cdot c_2^0}{f_1(c_1^1)}\left[\frac{f_1(c_1^0) - f_1(c_1^{*})}{f_1(c_1^{*})}\right], \qquad (9e)$$

Here, $f_1(c_1^1)$ represents the adsorption of substance 1 in the first adsorption wave – corresponding to concentration c_1^1. The width of the zone x_1 is given by the sum of x_2 and $x_{1,2}$:

$$x_1 = x_2 + x_{1,2}.$$

or, in accordance with Equations 9a and 9e:

$$x_1 = \frac{V_0 c_2^0}{f_1(c_1^{*})} + \frac{V_0 c_2^0}{f(c_1^1)}\ \frac{f(c_1^0) - f_1(c_1^{*})}{f_1(c_1^{*})}. \qquad (9f)$$

On the other hand, for the rate of movement of the first sorption wave we may write the following relationship:

$$\frac{V_0}{x_1} = \frac{f_1(c_1)}{c_1^1}$$

whence

$$x_1 = \frac{V_0 c_1^1}{f_1(c_1^1)} \qquad (9g)$$

Equating the R.H.S. of 9f and 9g we obtain the following equation for the concentration c_1^1 of the less readily sorbing substance 1 in the first adsorption wave:

$$c_1^1 = c_1^0 + c_2^0 + \frac{f_1(c_1^1) - f_1(c_1^0)}{f_1(c_1^{*})} \cdot c_2^0, \qquad (10)$$

or, in a somewhat modified form,

$$c_1^1 = c_1^0 + \left[1 + \frac{f_1(c_1^1) - f_1(c_1^0)}{f_1(c_1^{*})}\right]. \qquad (10a)$$

From Equation 10 it will be seen that the concentration c_1^1 of substance 1 in the first wave is greater than the sum of the influx concentrations $c_1^0 + c_2^0$ If we write

$$1 + \frac{f_1(c_1^1) - f_1(c_1^0)}{f_1(c_1^{*})} = \alpha, \qquad (11)$$

we obtain Yankovsky's formula:

$$c_1^1 = c_1^0 + \alpha c_2^0. \qquad (12)$$

The quantity α is the so-called coefficient of displacement of the first, less readily sorbing substance by the second from the surface of the adsorbent. Below, we shall show the effect of external parameters (total concentration $c = c_1^0 + c_2^0$ ratio of initial concentrations c_2^0/c_1^0 and temperature T) on the value of the displacement coefficient.

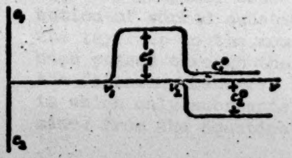


Fig. 5. Effluent curve (adsorption dynamics of a mixture of two substances for $c_2 \ll c_1$)

For the case considered, Fig. 5 shows the "effluent curve", which gives the relation between the volume V of the carrier that is passed through and the effluent concentrations c_1^0 and c_2^0. The value V_1 on this curve, which corresponds to the volume for which a layer of length x has "worked off" the first, less readily sorbing substance, may be determined from equations 9f and 9g by replacing V by V_1 and x_1 by x:

$$V_1 = \frac{x}{\frac{c_2^0}{f_1(c_1^*)} + \frac{c_1^0}{f_1(c_1^*)} + \frac{c_1}{f_1(c_1^*)} \cdot \frac{f_1(c_1^0) - f_1(c_0^*)}{f_1(c_1^*)}} \qquad (13)$$

or

$$V_1 = x \Big/ \frac{c_1}{f_1(c_1^*)} \; . \qquad (13a)$$

The value V_2 on the effluent curve (Fig. 5), which corresponds to the passage of the second, more readily adsorbed substance beyond the layer x, can be calculated from Equation 9a by replacing x_2 by x.

$$V_2 = \frac{x}{\frac{c_2^0}{f_0(c_1^*)}} \; . \qquad (14)$$

We will now examine in greater detail the effect of external parameters on the dynamics of adsorption.

Effect of the Sum of the Influx Concentrations $c_1 = c_1^0 + c_2^0$

Let us turn again to the initial graph (Fig.1). From this graph it follows that the character of the adsorption isotherm depends greatly on the relative disposition of the limits Q_1^1 and Q_1^*. So long as the composition of the original mixture does not change, the limit Q_1^* also remains unchanged. As the total concentration is diminished, with $c_2^0/c_1^0 = \text{const.}$, the region occupied by the first gas will be gradually diminished. When the mixture is diluted c_1^0/c_1^* times, where c_1^* is determined by Equation 8, the first substance practically ceases to be adsorbed, and only substance 2 will be on the surface of the adsorbent, consequently:

$$f_1(c_1^0, c_2^0) = 0 \qquad (15)$$

and

$$f_2(c_1^0, c_2^0) = f_2(c_2^0). \qquad (15a)$$

The isotherms 15 and 15a lead to the peculiar picture of the dynamics of adsorption represented in Fig. 6.

Two sorption waves move through the layer of sorbent. The less readily sorbing substance 1 is completely absent from the second sorption wave. The movement of this wave is accompanied by complete desorption of the less readily sorbing substance 1, and consequently the concentration c_1^1 of this substance in the first sorption wave may be considerably greater than the original concentration c_1^0. The distribution of sorbed substances over the length of the layer up to the moment when a volume V_0 has been passed through the charge is determined in the following manner: the width x_2 of the zone in which only substance 2 is adsorbed is determined from the equation:

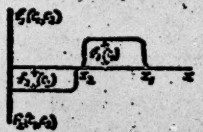


Fig. 6. Distribution of the adsorbed substances over the length of the layer for $c_2 > c_1$

$$\frac{V_0}{x_2} = \frac{f_2(c_2^0, c_1^0)}{c_2^0} \qquad (16)$$

Substituting for f_2 (c_1^0, c_2^0) from Equation 15a,

$$x_2 = \frac{V_0 c_2^0}{f_2(c_2^0)} . \tag{16a}$$

The region $x_{1,2}$ in which only substance 1 is sorbed is found from the following expression:

$$x_{1,2} = \frac{V_0 c_1^0}{\underline{f}_1(c_1^1)} . \tag{16b}$$

The total length of the layer, x_1, over which substance 1 is removed is given by:

$$x_1 - x_2 + x_{1,2} = \frac{V_0 \cdot c_2^0}{\underline{f}(c_2^0)} + \frac{V\ c_1^0}{\underline{f}_1(c_1^1)} \tag{16c}$$

On the other hand, the velocity of the first sorption wave is evidently given by the equation:

$$V_0/x_1 = \underline{f}_1(c_1^1)/c_1^1, \tag{16d}$$

whence

$$x_1 = \frac{V_0 \cdot c_1^1}{\underline{f}_1(c_1^1)} . \tag{16e}$$

Equating R.H.S. of Equations 16a and 16c we obtain

$$c_1^1 = c_1^0 + \frac{\underline{f}_1(c_1^1)}{\underline{f}_2(c_1^0)} . \tag{16f}$$

In this case, the displacement coefficient is defined as the ratio of the amount of substance 1 sorbed per unit length in the first sorption wave to the corresponding value for substance 2 in the second wave:

$$\alpha = \frac{\underline{f}_1(c_1^1)}{\underline{f}_2(c_2^0)} . \tag{17}$$

The effluent curve then has the form shown in Fig. 7. The value of V_1 on the effluent curve is determined from equations 16f and 16e by replacing V_0 by V_1:

$$V_1 = \frac{x}{c_2^0/\underline{f}_2(c_2^0) + c_1^0/\underline{f}_1(c_1^1)} \tag{18}$$

or.

$$V_1 = \frac{x}{c_1^1/\underline{f}_1(c_1^1)} . \tag{18a}$$

The value of V_2, which corresponds to the appearance of substance 2 beyond the layer $\underline{x}$ of adsorbent, is determined from Equation 16a by replacing x_2 by x:

$$V_2 = \frac{x}{c_2^0/f_2(c_2^0)} . \tag{18b}$$

Combining equations 18b and 18a with 16f we obtain:

$$c_1^0 = c_1^1 \left(1 + \frac{V_1}{V_2}\right) . \tag{19}$$

Equation 19 permits the initial concentration c_1^0 to be determined from the concentration c'_1, which is taken from the experimentally found effluent curve. The same curve enables V_1 and V_2 to be determined.

The ideas we have expressed concerning the effect of the sum of the influx concentrations $c = c_1^0 + c_2^0$ for constant c_2^0/c_1^0 are of fundamental importance for chromatographic practice. In fact, it is quite obvious that it is preferable to work according to the scheme represented in Fig. 6 than according to that of Fig. 4, for in the first case full separation into the components is attained already in the process of "composing" the chromatogram, and there is no need for the complex process of dynamic desorption ("development" of the chromatogram) that is usually applied in chromatography. The following is a practical conclusion arising from these considerations: before proceeding to the dynamic adsorption of a mixture of two substances having initial concentrations of c_1^0 and c_2^0, it is necessary to dilute with an inert carrier by $c_0^1/c_1^* = \gamma$ times, where c_1^* is determined by Equation 8.

It should be emphasized that owing to the steep exponential form of the relation between the saturation θ and the heat of adsorption Q the transition from scheme 4 to scheme 6 and back is very sudden; the quantity c_1^* is a sort of "critical" factor that completely determines the character of the dynamic adsorption process:

For $c_1^0 > c_1^*$ the adsorption dynamics follow the scheme of Fig. 4;

For $c_1^0 < c_1^*$ the adsorption dynamics follow the scheme of Fig. 6.

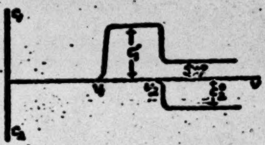


Fig. 7. Effluent curve (adsorption dynamic of a mixture of two substances for $c_2 > c_1$

Effect of the Ratio of Influx Concentrations c_2^0/c_1^0

The relative composition of the mixture c_2^0/c_1^0 determines the position of the internal boundary Q_1^* (Fig. 1). If the influx concentration c_1^0 is constant, then increase in the concentration c_2^0 of the second substance leads to its gradual predominance in the adsorbed phase. At a certain value $(c_2/c_1) = \delta_{crit}$, determined from the equation:

$$\delta_{crit} = (c_2/c_1)_{crit} = \frac{b_{02}}{b_{01}} e^{\frac{Q_1^*(\beta-1)}{RT}} , \qquad (4a)$$

the character of the dynamic adsorption process changes sharply:

for $Q_1^* < Q_1'$ the adsorption dynamics follow the scheme of Fig. 6;

for $Q_1^* > Q_1'$ the adsorption dynamics follow the scheme of Fig. 4.

Effect of Temperature T

In agreement with statistical theory [7,8], lowering of temperature moves the curves $b_1(Q_1)$ and $b_2(Q_2)$ downwards and to the left, in the direction of lower values of Q_1. At the same time, the boundaries of Q_1' (Fig. 1), separating the empty from the occupied regions, become sharper. When the concentration c_1^0 of substance 1 is constant, the boundary Q_1 is displaced by an amount that is proportional to the change in temperature:

$$Q_1^1 = RT \log \frac{b_{01}}{c_1^0} = \text{const } T . \qquad (20)$$

The law for the displacement of the internal boundary Q_1^* between the two occupied zones is easily obtained by suitable transformation of equation 4a:

$$Q_i = \frac{RT}{\beta - 1}\left[\log \frac{b_{02}}{b_{01}} - \log\left(\frac{c_2}{c_1}\right)_{crit}\right] . \tag{21}$$

It follows from Equation 21 that the logarithm of the critical ratio of concentrations at which the sharp transition occurs from predominance at the adsorbent surface of the first substance to predominance of the second is inversely proportional to the absolute temperature.

In other words, lowering of temperature at constant composition c_2/c_1 leads to a sharp transition from the dynamics scheme of Fig. 4 to the scheme shown in Fig. 6, even when the initial concentration ratio is unfavorable for separation.

Thus, the character of the dynamic process is very sensitive to temperature:

at $T < T_{crit}$, the process goes according to scheme 6,

at $T > T_{crit}$, the process goes according to scheme 4.

The sharp transition from one scheme of dynamic adsorption to another is characteristic only for an energetically heterogeneous surface. It is easy to show that in the case of the adsorption of mixtures that obey Langmuir's equation, which is typical for an energetically homogeneous surface, variations in the total and relative concentrations and in the temperature lead only to a gradual, smooth variation in the relative degrees of saturation of the surface by the components. As is well known, for the adsorption of mixtures according to Langmuir's equation the fractional saturations of substances 1 and 2 are expressed by the equations:

$$\theta_1 = \frac{c_1/b_1}{1 + c_1/b_1 + c_2/b_2} \tag{22a}$$

and

$$\theta_2 = \frac{c_2/b_2}{1 + c_1/b_1 + c_2/b_2} . \tag{22b}$$

For low saturation $c_1/b_1 + c_2/b_2 \ll 1$, and Equations 22a and 22b then lead to

$$\theta_1 = c_1/b_1 \tag{22c}$$

and

$$\theta_2 = c_2/b_2, \tag{22d}$$

i.e. at low saturation the adsorption of the components is not sensitive to the total concentration $c = c_1 + c_2$ and to the relative concentration c_2/c_1. It follows from Equation 22 that the ratio of the fractional saturations of the two components on a homogeneous surface is given by

$$\Delta = \frac{\theta_1}{\theta_2} = \frac{c_1}{c_2}\frac{b_2}{b_1} = \frac{c_1}{c_2}\frac{b_{02}}{b_{01}}e^{\frac{Q_1-Q_2}{RT}} . \tag{23}$$

Owing to the constancy of the difference $Q_1 - Q_2$, θ_1/θ_2 changes smoothly with change in c_1/c_2, without producing a sudden predominance of one of the components at definite critical values of c_1/c_2 It follows from Equation 22 that change in the temperature T also leads to smooth change in θ_1/θ_2; consequently, the phenomenon of a "critical temperature" (T_{crit}), which is characteristic for a heterogeneous surface, is now absent.

Hence, for a homogeneous surface in the region of low influx concentrations the picture to be expected of the dynamics of the adsorption is that represented diagrammatically in Fig. 4, according to which fractionation is only partly effected. In a large number of experimental researches into the low-temperature fractional desorption of mixtures of A, Kr, and Xe [9] and of hydrocarbon mixtures [10] the exceptional sensitivity of the separation process to the values of the total and relative concentrations of the components and to the temperature of desorption was established. It was established that for certain total and relative concentrations separation is possible, but for others it is not. Lowering of temperature has a marked effect on the efficiency: above a certain temperature, separation is impossible. These facts, and also the sensitivity that has been remarked in this work of the separation process to the order in which the components are introduced into the adsorption vessel, may be readily explained within the framework of the theory of adsorption at inhomogeneous surfaces.

The problem of the dynamics of the adsorption of mixtures at inhomogeneous surfaces is closely connected with the dynamics of the desorption of mixtures, which play a great role in chromatographic analysis. This question has a special interest of its own and will be examined in another paper.

SUMMARY

On the basis of statistical theory the following results have been obtained:

1. The effect of the heterogeneity of the adsorbent on the dynamics of the adsorption of a mixture of two substances has been investigated.

2. It has been shown that there is a possibility of sudden transitions from one course of dynamic adsorption to another at definite critical values of c, c_1/c_2, and T.

3. The conditions required for complete separation of a binary mixture at a heterogeneous surface have been established.

The ideas that have been brought forward are primarily interesting for the dynamics of the adsorption of mixtures at low saturations of the surface, for which heterogeneity is most strongly marked.

LITERATURE CITED

[1] M. M. Dubinin and S. Yavich, J. Appl. Chem., 9, 1191 (1936).

[2] M. M. Dubinin and Khrenova, Ibid., 9, 1204 (1936)

[3] O. M. Todes, Ibid., 18, 591 (1945)

[4] M. S. Tsvet. Chromatographic adsorption Analysis. (1946)

[5] S. Claesson, Arkiv för Kemi, Mineralogi och Geologi, 23 A, 1946

[6] M. M. Dubinin. Physicochemical Principles of Sorption Technology. 1935

[7] S. Z. Roginsky. Adsorption and Catalysis at Heterogeneous Surfaces. 1948

[8] S. Z. Roginsky and O.M. Todes. Problems of Kinetics and Catalysis, issue No. 7, 1949.

[9] K. Peters and Lohmar, Brennstoffchemie, 18, 41 (1937).
[10] Harteck, Ang. Chem. 53, 210 (1940).

Institute of Physical Chemistry
Academy of Sciences of the USSR

Received March 24, 1950

BLANK
PAGE

NEW METHOD OF SYNTHESIZING TRIALKOXYTITANIUM CHLORIDES

O. V. Nogina, R. Kh. Freidlina, and A. N. Nesmeyanov

Until recently, the only known compound of the type $(AlkO)_3TiCl$ has been triethoxytitanium chloride, prepared by the action of acetyl chloride on ethyl orthotitanate [1]. We have shown that triethoxytitanium chloride is obtained smoothly by the interaction of equimolecular quantities of pyridine hydrochloride and ethyl orthotitanate in a medium of benzene at 60-70° [2]. This observation permitted us to develop a method of direct synthesis of triethoxytitanium chloride by the reaction of $TiCl_4$ with ethanol in presence of pyridine in benzene medium. At the same time, ethyl orthotitanate and pyridine hydrochloride are formed, and in the subsequent heating of the reaction mixture these form triethoxytitanium chloride according to the equations:

$$4C_2H_5OH + TiCl_4 + 4C_2H_5N \rightarrow (C_2H_5O)_4Ti + 4C_5H_5N \cdot HCl;$$

$$(C_2H_5O)_4Ti + C_5H_5N \cdot HCl \rightarrow (C_2H_5O)_3\,TiCl + C_2H_5OH + C_5H_5N$$

In this way, triethoxytitanium chloride became a readily accessible substance [2]. However, this method does not appear to be a general one; attempts at preparing the triallyloxy- and tri-n-butoxytitanium chlorides and other such compounds were not successful [2]. Only the attempt to prepare tri-n-propoxytitanium chloride by treating n-propyl orthotitanate with pyridine hydrochloride was successful [3].

We considered that it might be possible to prepare trialkoxytitanium chlorides by transesterification (alcoholysis) of the accessible triethoxy compound by the action of alcohols according to the scheme:

$$(C_2H_5O)_3\,TiCl + 3ROH \rightleftarrows (RO)_3\,TiCl + 3C_2H_5OH.$$

The replacement of the last Cl in $(C_2H_5O)_3TiCl$ by an alkoxy group by the action of an alcohol must be very difficult, for it is known that in dichlorodialkoxytitaniums the further replacement of chlorine by alkoxy groups by the action of alcohols does not take place even with prolonged heating [1]. The application of the transesterification reaction to triethoxytitanium chloride met with difficulties, for it was found that under the required conditions replacement of chlorine by alkoxy occurs. Since trialkoxytitanium chlorides and alkyl orthotitanates containing the same alkoxy groups boil at similar temperatures, it was not found possible to separate them by distillation. Nevertheless, it was established by special experiments that even in the case of the higher alcohols, which distill off at a higher temperature, the replacement of Cl in $(AlkO)_3TiCl$ by an alkoxy group goes extremely slowly.

Thus, when 10 g of tri-n-hexyloxytitanium chloride is mixed with 50 ml of n-hexyl alcohol and the latter slowly distilled off, then HCl can be detected in the distillate, but even after repeating this procedure ten times, using 500 ml of n-hexyl alcohol, the reaction does not go to completion. If, however, in the above-described experiment triethoxytitanium chloride and ethyl alcohol are taken, then in the first 50 ml of the distillate no trace of HCl can be detected, and with further distillation only traces of chlorine can be detected in the distillate. In contrast with this extremely slow reaction, the transesterification reaction proceeds very rapidly. Hence, by observing definite conditions it was found possible to prepare various trialkoxytitanium chlorides practically free from contamination with the corresponding alkyl orthotitanates. These conditions comprise the conducting of the transesterification process at as low a temperature as possible and, in the case of the higher alcohols, also without continual addition of fresh portions of alcohol and, consequently, without their subsequent distillation. According to our observations, a two-fold excess of alcohol, taken at the beginning of the experiment, is sufficient.

The process of transesterification must be watched by making tests on the distillate for chlorine content or by introducing a solution of $AgNO_3$ in absolute alcohol in the receiver prior to the experiment. If HCl makes its appearance in the distillate, it is necessary to carry on distilling off the alcohol in a vacuum at a lower temperature. These precautions are particularly necessary when conducting transesterification with high-boiling alcohols. By this method we have succeeded in preparing the previously unknown tri-n-butoxy-, tri-isobutoxy-, tri-isoamyloxy-, tri-n-hexyloxy-, tri-β-chloroethoxy-, and tri-β-ethoxyethoxytitanium chlorides.

All the chlorides obtained, with the exception of tri-β-chloroethoxytitanium chloride, are colorless, transparent, viscous, hygroscopic liquids that may be distilled in a vacuum. The viscosity of the chlorides falls with increase in their molecular weight. Tri-β-chloroethoxytitanium chloride, both crude and doubly redistilled, is an extremely viscous (at room temperature) black mass

Thus, the proposed method is sufficiently general, and it is simple to carry out. The transesterification reaction requires very little time and gives an almost quantitative yield.

EXPERIMENTAL

All the experiments described below were carried out with completely dry starting substances and under conditions that prevented the admittance of moisture from the atmosphere.

Preparation of Tri-isoamyloxytitanium Chloride $(iso\text{-}C_5H_{11}O)_3TiCl$

A mixture of triethoxytitanium chloride (10 g = 0.046 mole) and isoamyl alcohol (25 g = 0.28 mole) was introduced into a Claisen flask connected to condenser and receiver. The apparatus was protected from the moisture of the air by a drying system. The reaction mixture was heated on an oil bath At a bath temperature of 140-150° a mixture of ethyl and isoamyl alcohols distilled off (b.p. 78-122°, 6.2g). When the temperature of the vapor reached 122°, the reaction mixture was cooled and further isoamyl alcohol (10 g) was added Distillation of the alcohol mixture then proceeded until the boiling point of isoamyl alcohol was reached; this indicated the end of the reaction. The excess of isoamyl alcohol was driven off in a vacuum. The product, which remained in the flask after driving off the alcohol, was distilled over at 174-175° at 2 mm. Yield 13.4 g, corresponding to 85% of theoretical.

On allowing the product to stand, a small number of crystals separated. On the assumption that these crystals consisted of a double compound of tri-isoamyl oxytitanium chloride and isoamyl alcohol, we heated the product in a vacuum (2 hr, 190-210°, 40 mm) in order to break up the double compound. During this time only a few drops of liquid distilled over The product was then distilled twice in vacuo from a Favorsky flask. The tri-isoamyloxytitanium chloride obtained is a colorless viscous hygroscopic liquid, boiling at 173.5-175° at 2 mm: n_D^{20} 1.5092; d_4^{20} 1.0600.

Found %: C 52.21; 52.15; H 9.78; 9.78; Ti 13.98; 14.05
$(C_5H_{11}O)_3TiCl$. Calculated %: C 52.25; H 9.64; Ti 13.89

Preparation of Tri-β-chloroethoxytitanium Chloride

The reaction between 10 g of triethoxytitanium chloride and 25 g of ethylene chlorhydrin was carried out as in the previous experiment A mixture of alcohols, boiling from 78 to 90°, was driven off, the bath temperature being 150°. The reaction mixture was cooled, and, after adding 10 g. of ethylene chlorhydrin, distillation was continued, the distillate being almost pure ethylene chlorhydrin. The excess of ethylene chlorhydrin was driven off in a vacuum. The residue distilled at 175-180° at 1.5 mm. Yield 10 g, corresponding to 67% of theoretical. Part of the product polymerized during distillation and remained in the distillation flask as a black powder; this explains the relatively low yield of product. On distilling a second time, the substance boiled at 194-196° at 2 mm. The doubly distilled product, as also the crude material, is a black extremely viscous hygroscopic mass.

Found %: C 22.40; 22.28; H 3.89; 3.84; Ti 14.29; 14.27
$(ClCH_2CH_2O)_3TiCl$. Calculated %: C 22.39; H 3.76; Ti 14.88

Preparation of Tri-n-butoxytitanium Chloride

The reaction between 8 g of triethoxytitanium chloride and 20 g of n-butyl alcohol was carried out as in the previous experiments. A mixture of alcohols, boiling from 100 to 113° was driven off, the bath temperature being 140°. After cooling the reaction mixture, n-butyl alcohol (12 g) was added, and distillation was continued. Almost pure n-butyl alcohol passed over, and the remainder was removed in a vacuum. The residue distilled at 145-148° at 2 mm. Yield 10 g, corresponding to 90% of theoretical. On distilling a second time, the product boiled at 154-155° at 2 mm. The chloride obtained is a colorless viscous hygroscopic liquid; n_D^{20} 1.5169; d_4^{20} 1.0985.

Found %: C 48.06; 47.98; H 9.03; 9.11; Ti 16.10; 15.84
$(C_4H_9O)_3TiCl$. Calculated %: C 47.61; H 8.99; Ti 15.82

Preparation of Tri-isobutoxytitanium chloride

Triethoxytitanium chloride (8.8 g) and isobutyl alcohol (25 g) were heated in a Claisen flask with condenser on an oil bath. The receiver contained a small amount of a solution of $AgNO_3$ in absolute alcohol. At a bath temperature of 120°, a mixture of alcohols started to come over. The first 10 ml of distillate contained only traces of chlorine, and then a further 10 ml was distilled over, and this showed a definite reaction for chlorine. The alcohol mixture and the excess isobutyl alcohol were then driven off at 48 mm. The residue distilled at 125-125.5° at 2mm. Yield 9.7 g, corresponding to 90% of the theoretical. On distilling a second time the product all came over at 147-148° at 5 mm. The tri-isobutoxytitanium chloride obtained is a transparent colorless extremely hygroscopic liquid; n_D^{20} 1.5158; d_4^{20} 1.1043.

Found %: C 47.81; 47.68; H 9.08; 9.13; Ti 15.55; 15.69
$(C_4H_9O)_3TiCl$. Calculated %: C 47.61; H 8.99; Ti 15.82

Preparation of Tri-n-hexyloxytitanium Chloride

The reaction between 10.3 g of triethoxytitanium chloride and 25 g of n-hexyl alcohol was carried out as in the previous experiment. At a bath temperature of 150°, practically pure ethyl alcohol distilled over. When 5.1 g of alcohol had distilled over (theoretical 6.4 g), distillation was continued at 44 mm to complete reaction and to remove excess of n-butyl alcohol. Both distillates gave positive reactions for chlorine. If distillation of the alcohols is carried out under more severe conditions, and fresh portions of alcohol are successively added, as usual for transesterification reactions, then appreciable amounts of n-hexyl orthotitanate are formed, and it is difficult to remove these, owing to the closeness of the boiling points of the two reaction products. The residue after removing excess n-hexyl alcohol distilled at 193-196° at 2 mm. Yield 17.7 g, corresponding to 97% of theoretical. On distilling a second time, the product boiled at 182-182.5° at 1 mm. This chloride is a slightly yellowish, comparatively mobile, hygroscopic liquid; n_D^{20} 1.5050; d_4^{20} 1.0039

Found %: C 56.30; 56.31; H 10.28; 10.31; Ti 12.12;
$(C_6H_{13}O)_3TiCl$. Calculated %: C 55.88; H 10.16; Ti 12.38

Preparation of Tri-β-ethoxyethoxytitanium Chloride

The experiment was conducted as indicated for the synthesis of triisobutoxytitanium chloride. From a mixture of 10.7 g of triethoxytitanium chloride and 25 g of ethyl cellosolve, 15 ml of alcohol mixture was distilled off. The distillate gave a reaction for chlorine. Further distillation of the mixture of alcohols and the excess of ethyl cellosolve was carried out at 45 mm. The doubly distilled product boiled at 182-183° at 1 mm; n_D^{20} 1.5178; d_4^{20} 1.2035. The yield is almost quantitative.

Found %: C 40.86; 40.91; H 8.11; 8.05; Ti 13.87; 13.71
$(C_2H_5OC_2H_4O)_3TiCl$. Calculated %: C 41.09; H 7.76; Ti 13.66

SUMMARY

1. A new method is proposed for the synthesis of trialkoxytitanium chlorides by transesterification of the readily accessible triethoxytitanium chloride according to the equation:

$$(C_2H_5O)_3TiCl + 3ROH \rightleftarrows (RO)_3TiCl + 3C_2H_5OH.$$

2. The following previously unknown trialkoxytitanium chlorides have been synthesized:

$(n-C_4H_9O)_3TiCl$,	b.p. 154 - 155°/2 mm
$(i-C_4H_9O)_3TiCl$,	b.p. 147 - 148°/5 mm
$(i-C_5H_{11}O)_3TiCl$,	b.p. 173 - 175°/2 mm
$(n-C_6H_{13}O)_3TiCl$	b.p. 182 - 182.5°/1 mm
$(ClCH_2CH_2O)_3TiCl$,	b.p. 194 - 196°/2 mm
$(C_2H_5OCH_2CH_2O)_3TiCl$	b.p. 182 - 183°/1 mm

LITERATURE CITED

[1] J. S. Jennings, Wardlaw, Way, J. Chem. Soc. 637 (1936).

[2] O.V. Nogina, R. Kh. Freidlina, and A. N. Nesmeyanov. Bull. Acad. Sci. U.S.S.R. Div. Chem. Sci., 3, 327 (1950)

[3] A. N. Nesmeyanov, R. Kh. Freidlina, and O. V. Nogina. Bull. Acad. Sci. U.S.S.R. Div. Chem. Sci., 3, 518 (1951)

Received September 17, 1951

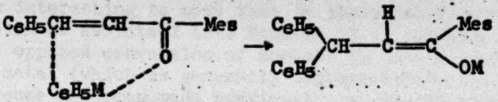
Institute of Organic Chemistry
of the U.S.S.R. Academy of Sciences

BLANK
PAGE

STEREOISOMERIC SODIUM ENOLATES

A. N. Nesmeyanov, B. A. Sazonova, and E. I. Vasilyeva

Like phenylmagnesium bromide [1] and phenyl-lithium [2], phenylsodium in benzene medium combines with benzylideneacetylmesitylene in the 1,4-position, forming a sodium enolate corresponding to the enol form of β,β-diphenylpropionylmesitylene. On benzoylating with benzoyl chloride, an enol-benzoate is formed, m.p. 162°. Comparison of the yields in the 1,4-addition reaction and the benzoylation leads to the conclusion that the whole of the sodium enolate is present in only one configuration, and the same conclusion is reached from the fairly high purity of the crude enol-benzoate obtained and from the impossibility of separating an isomeric O-benzoate from the benzoylation product. It is extremely probable that, as in the case of the 1,4-addition of phenyl-lithium and phenylmagnesium bromide, the configuration of the sodium enolate obtained in this way (we shall call it enolate I) is in accord with the following equation:



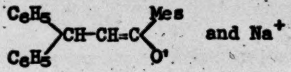
Addition of the molecule C_6H_5M (M is a metal) can be imagined to take place in such a way that the resulting benzhydryl and OM groups are in the cis positions to one another. The methoxymethylation of this enolate gives one of the two possible methoxymethyl O-derivatives, namely the liquid that is obtained from the 1,4-addition product of phenyl-lithium, and at the same time a C-methoxymethyl derivative, m.p. 154-155°, is formed. Thus, simultaneous reaction of the sodium enolate at O and at C is occurring.

The stereoisomeric sodium enolate (enolate II) can be obtained by the enolization of diphenylpropionylmesitylene by means of triphenylmethylsodium. Together with enolate II, a small amount of enolate I is formed. Thus, the enolization of diphenylpropionylmesitylene by triphenylmethylsodium occurs with the formation both of enolate I and of enolate II, the rate of formation of the latter being evidently considerably higher than the rate of formation of enolate I. On benzoylation with benzoyl chloride it gives mainly an enol-benzoate of m.p. 144°. Methoxymethylation leads to an O-derivative of m.p. 92-93°, stereoisomeric with the previous one, and at the same time it gives the same C-methoxymethyl derivative, m.p. 154°. Here again we have a sodium enolate that reacts in two ways – at O and at C.

Enolate II, although not of very low solubility in benzene (~ 5%) or ether (~ 8%) even at room temperature, is much less soluble than enolate I and is therefore relatively readily separated in the solid state. It crystallizes without solvent (benzene). It can be prepared in a pure form by heating enolate I on a boiling water-bath for 1-2 hrs. until as much as possible of the benzene present has been removed and then adding petroleum ether, which leads in the course of a day to the crystallizing-out of enolate II. On benzoylation, pure enolate II gives only the benzoate of m.p. 144°.

Thus, there are two steroisomeric Na derivatives of diphenylpropionylmesitylene, each of which gives only one of the two stereoisomeric benzoates of the enol form of diphenylpropionylmesitylene. It therefore follows that Enolates I and II are real enolates. With respect to benzoylation and methoxymethylation reactions, they behave like the previously described Li- and MgBr-enolates of diphenylpropionylmesitylene. Nevertheless, there are differences; these concern the considerably greater ease of the interconvertibility of the two sodium enolates. As stated above, Enolate I is converted into Enolate II on heating on a water bath. Under the same conditions Enolate II is partly converted into Enolate I, the reaction evidently tending to an equilibrium with a predominance of Enolate II. For this reason, all the above-described reactions of benzoylation and methoxymethylation were carried out at room temperature, at which no appreciable stereochemical conversion was to be observed; in any case, the rates of formation and of benzoylation of the sodium enolates formed in the two series of experiments are considerably greater than the rates of the cis-trans conversions.

It may be considered that the Na enolate dissociates on heating into ions:

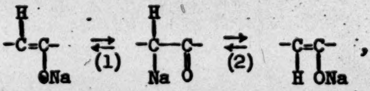


and that the stereoisomerization of the enolate proceeds through the ionization stage.

It is interesting to note that in presence of metallic sodium the rate of the conversion of Enolate I into Enolate II is reduced. Whether the cause for this is the opposed conversion of Enolate II into Enolate I under the action of the alkali metal (which is generally characteristic for cis-trans isomers), to which reference has been made previously, at present remains unexplained, in as much as Enolate II, on heating, is partly converted into Enolate I. Thus, the sodium enolates are considerably more labile than the lithium and particularly the magnesium enolates, which, of course, is not at all unexpected, though it makes it considerably more difficult to obtain reliable results.

Nevertheless, the fact of obtaining a definite enol-benzoate (or O-methoxymethyl derivative) by the benzoylation (or methoxymethylation) at room temperature of a definite stereoisomer of the enolate shows without doubt that these reactions proceed with non-ionized sodium enolates, for there would otherwise be obtained, in each case, either the same mixture of stereoisomers or just one stereoisomer – the more stable. The quaternary ammonium enolates behave in this way, which is shown in the previous and in the present work.

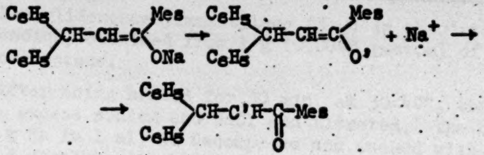
Thus, also in the case of sodium enolates must the hypothesis that explains the dual (at C and at O) reactivity by the reaction of a mesomeric anion be considered to be invalid. Also invalid, of course, is the suggestion that tautomeric conversion (reversible isomerization):



$$-\overset{H}{C}=\underset{ONa}{C}- \underset{(1)}{\rightleftarrows} -\overset{H}{\underset{Na}{C}}-\underset{O}{C}- \underset{(2)}{\rightleftarrows} -\underset{H}{C}=\underset{ONa}{C}- ,$$

is the cause of the dual reactivity of sodium enolates. If this were true under the conditions of the reactions studied, then equilibrium would be established in accordance with these equations (1 and 2), and benzoylation (and methoxymethylation) would lead to the same mixture of products whether Enolate I or Enolate II were employed. It is clear that the reagent did not act on a system in which an equilibrium had been established. In just the same way, it cannot be supposed that appreciable conversion of enolate into the keto form could occur in the reactions studied (C-methoxymethylation), to say nothing of the attaining of an equilibrium, and at the same time no conversion of the keto form into the stereoisomeric enolate (presence in the benzoylation or methoxymethylation products of only one stereoisomer of the enol derivative). If, indeed, for one moment we assume the formation of the keto form, then evidently, under the conditions of the equilibrium that would be assumed in this case, the enol forms would predominate, and the rate of keto-enol conversion would be greater than that of the reverse reaction. Thus, if the keto form were formed, the second enol form would be produced in great quantity and, under the conditions of the experiment, would be found in the form of esters or ethers. This conclusion is in accord with the result of C-alkylation of acetoacetic ester in aqueous alkaline medium [3].

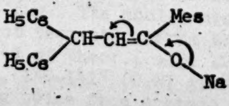
Again, experiment rejects the supposition, which is improbable in itself and is contradictory to the usual concepts, that first of all a sodium ion dissociates, and then a slow isomerization (electrono-isomerization) of the anion occurs (more slowly than the reaction with benzoyl chloride):



and finally reaction occurs at the C atom. If under the conditions of the reaction of a ketone-anion of this sort were formed, then there would be no reason why electrono-isomerization at at least the same rate should not occur into the stereoisomeric enolate anion, the presence of which would be revealed by the benzoylation or methoxymethylation.

Thus, replacement of the Na cation by the $C_6H_5(CH_3)_3N$ cation (which is known to be incapable of being covalently bound and is certain, therefore, to form an ionic system) in Na enolates I and II and subsequent benzoylation leads in both cases to a mixture of stereoisomeric enol-benzoates. If the enolate (after replacing the Na cation by $C_6H_5(CH_3)_3N^+$) is methoxymethylated, then again a mixture of stereoisomeric O-derivatives is formed; at the same time, the ammonium enolate, in contrast with the Na enolate, does not give a C-derivative. The alkylation and acylation of the ammonium enolates of carbonyl compounds will be the subject of a future investigation.

Thus, the most natural concept concerning the cause of the dual reactivity (at O and at C) of metal enolates still remains, in our opinion, after considering the results of experiments with sodium enolates, the concept that we have brought forward concerning the transfer of the reactive center of the molecule along the system of conjugated (Na–O)- and (C=C)-bonds:



When an electrophilic reagent attacks at C, the electron pair of the future covalent bond is called away from the oxygen to the carbon, as shown by the arrows. In our opinion, the picture as a whole becomes quite convincing on comparing our results on magnesium, lithium, sodium and ammonium enolates.

At first glance, the unexpected orientation (from the point of view of our hypothesis) of the methoxymethylation of an ammonium enolate (as distinct from MgBr, Li, and Na enolates) only on to O merits attention. An interesting parallel is the O-acetylation of acetoacetic ester in pyridine. Discussion of this question would be premature, for there are too few data, but we hope to turn to it later.

In connection with our present series of experiments, the natural question arises concerning the character of the dual (keto and enol) reactivities of keto and enol compounds. We suppose that in a large number of cases in which keto compounds react in enol-fashion (and enols in keto-fashion) the reaction proceeds with transfer of the reactive center without preliminary tautomeric change. This concerns, above all, cases of so-called pseudomerism.

EXPERIMENTAL

I. Addition of Phenylsodium to Benzylideneacetylmesitylene

Benzylideneacetylmesitylene (3 g) in absolute benzene (10 ml) is added to phenylsodium, obtained from 1 g (0.0043 g-atom) of sodium and 2.25 (0.02 mole) of chlorobenzene.

After being heated for 30 min. at 30-40°, the enolate solution is filtered from excess sodium and NaCl and titrated. The benzene solution (23 ml; 0.0077 g Na in 1 ml) is decomposed and washed with water; the benzene is driven off, and absolute alcohol is added to the residue.

Yield of β,β-diphenylpropionylmesitylene: 1.9 g (75% of theoretical); m.p. 78-79°. After two crystallizations from alcohol: m.p. 80-81°. Mixed test with known diphenylpropionylmesitylene melts without depression.

II. Benzoylation of the Na Enolate[1] Produced by the 1,4-Addition of Phenylsodium to Benzylideneacetylmesitylene

Benzoyl chloride (0.94 g) in absolute benzene (2 ml) is added to 22 ml of a solution of Na enolate I (0.0070 g Na per ml). The reaction mixture is decomposed by water, the benzene layer is washed with water, the benzene is driven off, and acetone is added to the residue. The crystals that separate are filtered off and washed with acetone. Yield of enol-benzoate: 2.37 g (80% of theor.); m.p. 156-157° (before recryst.). After recrystallization from acetone: m.p. 161-162°. Mixed test with benzoate of m.p. 162° (prepared by the benzoylation of the MgBr enolate) melts without depression.

III. Heating (80°) of Na Enolate I

1. Without metallic sodium. A benzene solution of Na enolate I (24 ml; 0.0071 g Na per ml) was boiled for 1.5 hr and then benzoylated. The reaction mixture was decomposed with water, the benzene was evaporated off, and acetone was added to the residue. The enol-benzoate isolate (0.9 g: 28% of theor.) melts at 158-160° (not recryst). From the acetone solution a mixture of enol-benzoates (1.42 g: 44% of theor.; m.p. 122-123°) was obtained; from this an enol-benzoate of m.p. 140-141° (0.27 g: 8% of theor.) was separated; m.p. after recrystallizing twice from acetone – 144°.

---

[1] This Na enolate will be called in future Na enolate I, and the isomeric enolate, Na enolate II.

2. In presence of metallic sodium. Metallic sodium (0.15 g) was added to 22 ml of a benzene solution of Na enolate I, and the mixture was heated at 80 deg for 1.5 hr. After benzoylation and suitable treatment, as described in the previous experiment, an enol-benzoate (1.45 g, 49% of theor.) of m.p. 156-158° (after recrystallization 159-160°) and a mixture of benzoates (0.7 g: 24% of theor.) were obtained by fractional crystallization of the mixture an enol-benzoate (0.15 g: 5% of theor.) of m.p. 140-141° (144° after double recrystallization) was separated.

IV. Methoxymethylation of Na Enolate I

Chloromethyl methyl ether (2.4 g: 100% excess) in absolute benzene (2 ml) is added to 35 ml of a benzene solution of enolate I (0.0095 g Na per ml). The reaction mixture is decomposed with an aqueous solution of caustic soda, the benzene layer is washed with water, the benzene is evaporated off. The precipitated crystals are filtered from the oil and washed with petroleum ether. Yield of C-methoxymethyl derivative: 2.26 g (42% of theor.); m.p. 151-152°. M.p. after recrystallization from methyl alcohol: 154-155°. Mixed test with known sample showed no depression of m.p. Data in literature: m.p. 155° (Kohler [5]; Nesmeyanov and Sazonova [2]).

After evaporating off the petroleum ether, the oil was distilled in a vacuum: b.p. 215-217°, 2.5 mm. Yield of the O-methoxymethyl derivative of diphenylpropionylmesitylene: 1.84 g (34% of theor.). On introducing nuclei of solid O-derivative, crystallization did not set in. Data in literature: b.p. 216-218°, 3 mm [2].

V. Hydrolysis of the Liquid O-Methoxymethyl Derivative

The liquid O-methoxymethyl derivative of diphenylpropionylmesitylene (0.59 g) was boiled with 10 ml conc. HCl for 1 hr. (after boiling for a few minutes the aqueous solution gives a reaction with fuchsin-sulfurous acid). The mixture was diluted with water, the oil extracted with ether, and the ether driven off. M.p. after recrystallization from alcohol: 80°. Yield of β,β-diphenylpropionylmesitylene: quantitative. After repeated recrystallization, m.p. 81-82°. Mixed m.p. with known sample showed no depression.

VI. Reaction of Na Enolate I with Trimethylphenylammonium Benzenesulfonate

1. Benzoylation. A benzene solution of Na enolate I (29 ml; 0.0070 g Na per ml) is divided into two parts. To one is added trimethylphenylammonium benzenesulfonate (2.7 g: 100% excess). Each portion is stirred at room temperature for one hour and then benzoylated.

a) From the portion without ammonium salt (14 ml of enolate solution) the following were separated after benzoylation: 1.47 g (79% of theor.) of enol-benzoate, which after recrystallization from acetone has m.p. 161-162° (not recryst: 155-156°), and 0.02 g of a mixture of enol-benzoates, m.p. 123-127°.

b) The portion with ammonium salt (15 ml of enolate solution) was treated in the following way. The precipitate was filtered off, carefully washed with benzene, dried in a stream of dry nitrogen, and analyzed for Na:

Found %: Na 0.94; 0.88.

This points to the presence in the precipitate of sodium benzenesulfonate formed as a result of double decomposition of the salts.

The filtrate was benzoylated and there were obtained as products: 0.33 g (16% of theor.) enol-benzoate of m.p. 154-155°, melting, after recrystallization from acetone, at 161°, and 0.72 g (37% of theor.) of a mixture of enol-benzoates of m.p. 122-125°, from which, by fractional crystallization, an enol-benzoate of m.p. 140-141° (0.14 g: 7% of theor.) was separated. After recrystallization from acetone the m.p. of the substance obtained and the mixed m.p. of a mixed test with a known sample was 143-144°. On hydrolyzing the mixture of enol-benzoates (m.p. 122-125°), β,β-diphenylpropionylmesitylene was obtained in 97% yield[1].

2. Methoxymethylation. Trimethylphenylammonium benzenesulfonate (9g: 25% excess) is added to 46 ml of a benzene solution of Na enolate I (0.017 g-atom Na per ml). The reaction mixture is stirred for 2.5 hr at room temperature, then chloromethyl methyl ether (13.6 g: 100% excess) in 20 ml of absolute benzene is added, and the mixture is allowed to stand for 1 hr. After decomposition with aqueous alkali, washing the benzene layer with water, and evaporation of the benzene, no C-derivative was obtained. A solid O-derivative (2.0 g) of m.p. 81° was separated from the oil. After the O-derivative had been recrystallized from alcohol, it melted at 90°, both alone and when in admixture with a known sample. Yield 1.8 g (20% of theor.).

The oil that had not crystallized was vacuum-distilled: b.p. 218-220°/3 mm. Yield of liquid O-derivative, stereoisomeric with the previous one: 5.05 g (56% of theor.).

VII. Enolization of β,β-Diphenylpropionylmesitylene by Phenylsodium, and Subsequent Benzoylation

1) β,β-Diphenylpropionylmesitylene (2 g) in 10 ml of absolute benzene is added to phenylsodium prepared from 0.7 g (0.03 g-atom) of sodium and 1.37 g (0.012 mole) of chlorobenzene. The reaction mixture is warmed for 30 min., after which time an addition is made of 2.14 g of benzoyl chloride. The mixture is decomposed with water, the benzene layer is washed, the benzene is driven off, and acetone is added to the residue. The crystals are filtered off and washed with acetone. A mixture of the cis and trans isomeric enol-benzoates, m.p. 123-126°, is obtained. Yield 1.95 g (75% of theor.). M.p. unchanged by recrystallization.

Found %: C 86.08, 86.04; H 6.75, 6.67.
$C_{31}H_{28}O_2$. Calculated %: C 86.07; H 6.52.

A benzoate of m.p. 160-161° (0.2 g) and a benzoate of m.p. 143-144° (0.2 g were isolated from the mixture obtained.

2) Hydrolysis of the mixture of benzoates: the mixture of benzoates of m.p. 123-126° (1 g) was boiled for 30 min. with an alcoholic solution containing 0.2 g of caustic soda, and the mixture was then diluted with water, the oil was extracte with benzene, the benzene solution was washed with water, and the benzene was evap orated off. Absolute alcohol was added to the residue and the crystals that separated were filtered off; m.p. 80-81°. Yield of β,β-diphenylpropionylmesitylene 0.74 g (98% of theor.).

VIII. Enolization of β,β-Diphenylpropionylmesitylene by Metallic Sodium, and Subsequent Benzoylation

Diphenylpropionylmesitylene (1 g) in 10 ml of absolute toluene was boiled with 0.15 g of metallic sodium for 2 hr, and benzoyl chloride (0.35 g) was then added (solution first poured off metallic sodium).

---

[1]) The benzoate of m.p. 162° is not converted into a mixture of cis and trans isomeric enol benzoates under the action of trimethylphenylammonium benzenesulfonate.

The reaction mixture was decomposed with water, the toluene layer was washed with water, and the toluene was evaporated off. The crystals that separated after adding acetone were filtered off and washed with acetone. The products obtained were 0.22 g (17% of theor.) of an enol-benzoate of m.p. 154-156°, recryst. m.p. 160-161°, and 0.26 g of a mixture of enol-benzoates, m.p. 124-126°, from which, by fractional crystallization, an enol-benzoate of m.p. 140-141° (0.07 g: 5% of theor.) was separated - m.p. after two recrystallizations 144°. The total yield of enol-benzoates was 37% of theoretical.

IX. Conversion of α-Bromo-β,β-diphenylpropionylmesitylene into Enolate I by the Action of Phenylsodium, and Subsequent Benzoylation[1]

α-Bromo-β,β-diphenylpropionylmesitylene (3 g) in 30 ml of absolute benzene is added to phenylsodium prepared from 0.85 g (0.037 g-atom) of sodium and 1.67 g (0.015 mole) of chlorobenzene. After heating for 1 hr at 40-50°, benzoyl chloride (2.6 g) is added, and the mixture is heated for a further half hour. The separation of the benzoate is described above; m.p. 155-157° (not recryst.). Yield 1.35 g (42% of theor.). After recrystallizing twice from acetone, m.p. 162°.

X. Enolization of β,β-Diphenylpropionylmesitylene by means of Triphenylmethylsodium

1) Benzoylation. β,β-Diphenylpropionylmesitylene (1.2 g) is added to 45 ml of an ethereal solution of triphenylmethylsodium containing 0.022 g of $(C_6H_5)_3CNa$ per ml; then benzoyl chloride (0.51 g) is added. The mixture is decomposed with water, the ethereal solution is washed, and the ether is evaporated off. The crystals that separate after adding acetone are filtered off and washed with acetone. An enol-benzoate (0.95 g: 60% of theor.) of m.p. 134-136° is obtained. After recrystallizing from acetone it melts at 143-144°, both alone and in admixture with known material. After removing triphenylmethane from the mother liquor, a mixture of enol-benzoates (0.25 g) of m.p. 124-125° was separated.

2) Methoxymethylation of Na enolate II. β,β-Diphenylpropionylmesitylene (2.25 g) is added to 54 ml of an ethereal solution of triphenylmethylsodium (0.035 g per ml); chloromethyl methyl ether (1.2 g: 100% excess) is then added. The mixture is decomposed with an aqueous solution of caustic soda, the ethereal layer is washed with water, the ether is distilled off, and petroleum ether is added to the residue. The crystals that separate are filtered off and recrystallized from methanol. The C-methoxymethyl derivative, m.p. 153-154°, is obtained. Yield 1.2 g (47% of theor.): a mixed test with known C-derivative gave no depression of m.p. After evaporating off the petroleum ether, the residue was recrystallized from benzene, m.p. 91-92°. Mixed test with triphenylmethane melted at 91-92°.

The O-methoxymethyl derivative of diphenylpropionylmesitylene (0.2 g: 8% of theor.) was separated from the filtrate after removal of benzene. The m.p. after recrystallization from methanol was 92-93°. A mixed test with known O-derivative showed no depression of m.p. A mixed test with triphenylmethane gave m.p. 67-70°. Data from literature: m.p. 92° [5], 92-93° [2].

XI. Hydrolysis of the Solid O-Methoxymethyl Derivative

This substance (0.30 g) was boiled with 8 ml of conc. HCl for 1 hr (the aqueous solution gives, after a few minutes' boiling, a reaction with fuchsin-sulfurous acid). The reaction mixture was diluted with water, the oil was extracted with ether, the ether was evaporated off, and the residue was recrystallized from absolute alcohol, m.p. 81-82°. Yield of diphenylpropionylmesitylene 0.25 g (96% of theor.).

---

[1] In the case of the magnesium derivative of diphenylpropionylmesitylene, this method yields MgBr enolate II [4].

XII. Isolation of Na Enolate II. Its Properties.

The benzene solution of Na enolate I, obtained by adding phenylsodium to benzylideneacetylmesitylene, is filtered from Na and NaCl. The benzene is driven off and the residue is heated for 2 hr on a boiling water-bath (Na enolate I is converted by heat into Na enolate II); petroleum ether is then added, and the solutio is left for 24 hr for the crystallization of Na enolate II to occur. The precipitated crystals are filtered off, washed 4 times with petroleum ether, and dried by the prolonged passage of a stream of pure dry nitrogen.

Na enolate II is in the form of crystals of a slightly yellow color. It is fairly soluble in ether (8 g in 100 ml of ether at 20°), rather less in benzene (5 g in 100 ml of benzene at 20°).

Found %: Na 6.68; 6.55
$C_{24}H_{23}ONa$. Calculated: Na 6.56

1) Na enolate II (0.39 g) was decomposed with water, the oil was extracted with benzene, and the benzene was evaporated off. Absolute alcohol was added to the residue. Yield of β,β-diphenylpropionylmesitylene 0.34 g (95% of theor.); m.p. 79-80°. After two recrystallizations from alcohol m.p. 81-82°.

2) Benzoylation. Enolate II (0.846 g) and absolute benzene (5 ml) were mixed for 1 hr at room temperature (for better dissolution), and then benzoyl chloride (0.34 g) was added. After the usual treatment the enol-benzoate (0.719 g; 6% of theory) of m.p. 140-141° was separated. After recrystallizing twice from acetone, it melted at 144-145°.

3) Conversion of Na enolate II into Na enolate I. Na enolate II (0.282 g) in 5 ml benzene was boiled for 1.5 hr and then benzoylated. A mixture of enol-benzoates (0.230 g: 72% of theor.) was obtained, and from these an enol-benzoate (0.03 g: 9% of theor.) of m.p. 159-160° (recryst. 160-161°)was separated.

XIII. Reaction of Na Enolate II with Trimethylphenylammonium Benzenesulfonate

Na enolate II (1.364 g) and trimethylphenylammonium benzenesulfonate (2.3 g: 100% excess) were stirred in benzene for 1 hr at room temperature. After benzoylation, a mixture of enol-benzoates (1.037 g: 62% of theor.) was obtained, and from this an enol-benzoate (0.28 g: 16% of theor.) of m.p. 157-158° (double recryst: 160-161°) and an enol-benzoate (0.12 g: 7% of theor.) of m.p. 140-141° were isolated; the latter, after recrystallizing twice from acetone gave a m.p. and a mixed m.p. of 144-145°.[1]

SUMMARY

1. It has been shown, on the basis of β,β-diphenylpropionylmesitylene as example, that the sodium derivatives of keto compounds exist in two cis - trans stereoisomeric forms, and that they are therefore enolates.

---

[1] 1-Benzoylation of Na enolate II (blank experiment), see Expt. XII, 2; 2 - the benzoate of m.p. 144° when submitted to the action of triphenylmethylammonium benzenesulfonate is not converted under the same conditions into a mixture of cis and trans isomeric enol-benzoates.

2. On benzoylating the stereoisomeric Na enolates at room temperature, the corresponding stereoisomeric enol-benzoates are formed. On methoxymethylating, they give the corresponding stereoisomeric O-methoxymethyl derivatives together with one form only of C-methoxymethyl derivative.

3. On replacing Na by $(CH_3)_3C_6H_5N^+$, the stereoisomers, instead of reacting differently, react in identical fashion (with benzoyl chloride and chloromethyl methyl ether). Also, a C-methoxymethyl derivative is not formed.

4. It has been shown that the sodium enolates are considerably more labile than the lithium and, particularly, the magnesium enolates, which were studied previously. Thus, on heating, the sodium enolates are mutually converted, giving a mixture in which the more stable enolate predominates.

5. As in the case of the Li and MgBr enolates, the conclusion is reached that the dual reactivity (alkylation or acylation on O and on C) of Na enolates is, in the first place, not due to the reversible isomerization (tautomerization) of these enolates into a keto form containing a C-metal bond and, in the second place, not due to the presence of an ionic structure in these enolates and to dual reactivity in the mesomeric ion.

6. The hypothesis previously put forward concerning the transfer of the reactive center of the molecule along a system of conjugated (Na – O and C=C) bonds as the cause of the dual reactivity (at O and at C) of metal enolates is confirmed.

M.V.Lomonosov Moscow State University Received July 12,1951

LITERATURE CITED

[1] A.N.Nesmeyanov, V.A.Sazonova, and E.B.Landor. Proc.Acad.Sci.USSR, 63, 4, 395, (1948).

[2] A.N.Nesmeyanov, V.A.Sazonova. Bull.Acad.Sci.USSR. Div.Chem.Sci., 4, 422, (1949).

[3] I.L.Knunyants. J.Gen.Chem., 69, 7, 2852 (1937).

[4] E.P.Kohler, M.Tishler, H.Potter. J.Am.Chem.Soc., 57, 2517 (1935).

[5] E.P.Kohler, Thompson. J.Am.Chem.Soc., 59, 887 (1937).

BLANK
PAGE

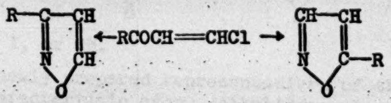
SYNTHESIS OF ISOXAZOLES FROM β-CHLOROVINYL KETONES

N.K.Kochetkov, A.N.Nesmeyanov, and N.A.Semenov.

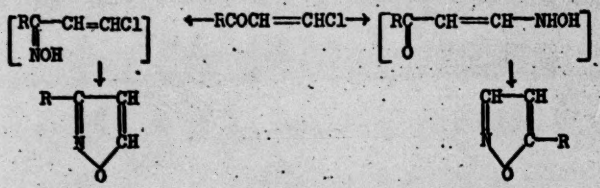
As we have recently shown [1], methyl β-chlorovinyl ketone is a convenient starting material for the synthesis of various heterocyclic compounds, including methylisoxazole. On the basis of this reaction we have developed a new general method for the synthesis of alkylisoxazoles, which have until now been practically unstudied owing to their inaccessibility.

The reaction of alkyl β-chlorovinyl ketones, which are readily prepared by the method described by us in conjunction with Rybinskaya [2], with hydroxylamine hydrochloride is most conveniently carried out in methanol, although other solvents, such as acetic acid, may be used. The lower alkylisoxazoles (methyl- and ethyl-) are appreciably volatile in alcohol vapor and are soluble in water, and therefore in separating them from the reaction mixture we made use of the ability of isoxazoles to give crystalline complexes with cadmium chloride [3]; using these complexes, we separated them in much the same way as we have described for methylisoxazole [1]. On the other hand, the higher homologs are of low solubility in water, and their separation can be carried out without difficulty by the usual method. We have prepared by the method described methyl-, ethyl-, propyl-, and isobutylisoxazoles with yields of 60-70%.

On treating our methylisoxazole with sodium ethoxide in ether, following Claisen [4], cyanoacetone was separated in the form of its sodium salt; it was identified by conversion into the phenylhydrazone. This proves the presence of α-methylisoxazole in the substance that we obtained. From the reaction mixture, after removing the sodium salt of cyanoacetone, we isolated pure γ-methylisoxazole. Using the procedure developed by Claisen [4], we determined the content of α-isomer in the alkylisoxazoles that we obtained (from the weight of the salt of the corresponding cyanoketone that was separated); it varied from 60 to 68%. Thus, it was shown that the alkylisoxazoles that we obtained were mixtures of γ- and α-isomers:

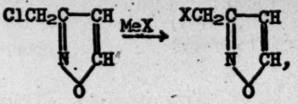


The question of the mechanism of the simultaneous formation of the two isomers was not specially investigated by us. It is most probable that the formation of a mixture of isomers is brought about by two competing reactions:



However, another possibility is not altogether excluded, namely that alkyl β-chlorovinyl ketone at first goes over into some sort of intermediate compound, which then gives α- and γ-isomers simultaneously. The intermediate compound could be either the so-called "sesquioxime", which has been shown [5] to be formed intermediately in the synthesis of isoxazoles from hydroxymethylene ketones, or the acetal of a β-ketoaldehyde, which, as shown by us and Rybinskaya [6], is readily formed by the action of alcohol on a β-chlorovinyl ketone; in our case, alcohol was used as solvent.

By using the method we have developed for the synthesis of isoxazoles, we were able to obtain, apart from alkylisoxazoles, previously inaccessible isoxazoles containing halogen in the side-chain. For this purpose we used the reaction of chloromethyl β-chlorovinyl ketone with hydroxylamine, and obtained as a result chloromethylisoxazole. The procedure for the synthesis of chloromethyl β-chlorovinyl ketone from chloroacetyl chloride, given by English authors [7], was improved by us, and the yield of chloromethyl β-chlorovinyl ketone was raised to 80%. This compound by reaction with hydroxylamine under the usual conditions gives chloromethylisoxazole with a yield of 85%. It was found, unexpectedly, that the substance obtained was not split with sodium alkoxide, which points to the absence therein of α-isomer and gives us the right to regard it as pure γ-chloromethylisoxazole. This compound is very interesting in connection with the synthesis of completely inaccessible isoxazole derivatives, which have recently assumed practical importance as physiologically active substances. As was to be expected, the Cl atom in γ-chloromethylisoxazole is very readily replaced by nucleophilic groups. Thus, reaction with NaBr and NaI leads to bromo- and iodo-methylisoxazole, and reaction with NaCN in alcohol gives 3-isoxazole-acetonitrile, which can act as starting material for further interesting syntheses:



where X = Br, I, or CN.

All the newly prepared representatives of the isoxazole class are mobile liquids of characteristic odor. Alkylisoxazoles very slowly darken on storing. In the calculation of the molecular refractions of the compounds prepared we used Auwers' data [8], but in all cases obtained low values in comparison with the calculated values. This shows that the increment recommended by Auwers for nitrogen in the isoxazole ring (3.901) is not satisfactory and requires revision. In fact, the mean departure for the isoxazoles prepared by us and also for the previously known representatives of this series, which were used by Auwers for his calculations, is 1.19. Auwers assumes for the nitrogen increment of isoxazoles the value for aliphatic oximes, and the departure of the values found from the calculated values he regards as "negative exaltation". Such a point of view is hardly valid.

The cyclic system of isoxazole has a number of peculiarities that bring it close to aromatic compounds, which may be illustrated, for example, by the ease of electrophilic substitution reactions. It is quite natural, therefore, that an atom of nitrogen, when contained in the isoxazole system, should acquire a quite different character, sharply differentiated from the character of a nitrogen atom in an aliphatic oxime. The calculations we have made show that more satisfactory agreement is obtained between the values for the molecular refractions of isoxazoles when the value of the nitrogen increment is assumed to be that of the nitrogen of a tertiary amine (2.84).

EXPERIMENTAL

I. Chloromethyl β-Chlorovinyl Ketone

Aluminum chloride (180.0 g) is added gradually over 1 hour with energetic stirring to 113.0 g of chloroacetyl chloride, and acetylene is passed in a rapid stream for 6 hours; the temperature of the reaction mass is maintained at 25-35°. The reaction mass is poured on to ice and extracted with ether; the extract is dried over calcium chloride; the solvent is driven off, and the residue is vacuum-distilled, the fraction boiling at 62-65° at 8-10 mm being collected. Yield 87.7 g (84% of theoretical, calculated on aluminum chloride, 65% of theoretical, calculated on chloroacetyl chloride). The pure substance has b.p. 58-59°/7 mm; 73-75°/15 mm. (Data in literature: [7]): 71-74°/10 mm; [9] 71-72.5°/12 mm).

II. Methylisoxazole

Methyl β-chlorovinyl ketone (24.0 g) is added to a solution of 15.0 g of hydroxylamine hydrochloride in 200 ml of methanol, and the mixture is heated for 3 hours on a water-bath. A saturated aqueous solution of cadmium chloride (80 g) is then added to the hot mixture, and the mixture is then again heated to boiling and left to stand overnight. The precipitate of the complex is filtered off, washed with a solution of cadmium chloride, transferred wet to a Wurtz flask, and there decomposed by heat. The distillate is saturated with sodium sulfate, the oily layer of methylisoxazole is separated, and the aqueous layer is extracted with ether. The extract, united with the main portion of the substance, is dried over magnesium sulfate, the ether is driven off, and the residue is distilled from a Favorsky flask with a good fractionating column. Yield 11.2 g (58.4% of theoretical). After a second distillation the substance has the following constants: b.p. 118-122°; d_4^{20} 1.0283; n_D^{20} 1.4380; found MR_D 21.21; for $C_4H_5ON \vDash$ calculated MR_D (according to Auwers) 22.45; calculated MR_D (nitrogen increment 2.84) 21.39. (Data in literature [8]: α-methylisoxazole, b.p. 122°; d_4^{20} 1.023; n_D^{20} 1.439; γ-methylisoxazole, b.p. 118°; d_4^{20} 1.022; n_D^{20} 1.435).

Found %:	C 57.84; 57.76;	H 6.20; 6.10;	N 17.00; 16.95;
C_4H_5ON. Calculated %:	C 57.85;	H 6.03;	N 16.86.

Methylisoxazole is a colorless mobile oil with an odor reminiscent of that of pyridine. It is fairly soluble in water. It may be preserved for a long period without change.

III. Treatment of Methylisoxazole with Sodium Ethoxide

Methylisoxazole (10.0 g) is treated in the cold with a solution of sodium ethoxide prepared by dissolving 2.5 g of sodium in 50 ml of alcohol; absolute ether (40 ml) is then added. After 1 hour the precipitated sodium salt of cyanoacetone is filtered off; the filtrate is neutralized with hydrochloric acid to phenolphthalein and extracted with ether. The ether is driven off, and a saturated aqueous solution of cadmium chloride is added to the residue. After 2 hours, the precipitate of the complex is filtered off and decomposed by heat, while still in the wet condition, in a Wurtz flask. The distillate is extracted with ether, the extract is dried over megnesium sulfate, and the ether is driven off. On distilling the residue, γ-methylisoxazole (2.3 g) was obtained; it gave no precipitate on treatment with sodium ethoxide. The substance has b.p. 118°; d_4^{20} 1.0206; n_D^{20} 1.4348. (Data in literature: [8]): b.p. 118°; d_4^{20} 1.022; n_D^{20} 1.435.)

A small amount of the sodium salt of cyanoacetone was dissolved in aqueous acetic acid and phenylhydrazine was added; the precipitate formed was filtered off and, after recrystallization from alcohol, was obtained as colorless crystals m.p. 100° (data in the literature for the phenylhydrazone of cyanoacetone: [5] m.p. 101-102°; [10] m.p. 96-97°).

The same experiment was carried out quantitatively: from 4.620 g of methylisoxazole 4.008 g of the sodium salt of cyanoacetone was obtained, corresponding to a content in the mixture of 68% α-isomer.

IV. Ethylisoxazole

This was prepared and isolated analogously to methylisoxazole (Section II) from 5.6 g of hydroxylamine hydrochloride and 9.2 g of ethyl β-chlorovinyl ketone in 70 ml of methanol. Yield 4.55 g (60% of theoretical). After redistilling, the ethylisoxazole had the following constants: b.p. 139-140°; d_4^{20} 0.9916; n_D^{20} 1.4440; found $\underline{\underline{MR}}_D$ 26.02; for $C_5H_7CN\models$ calculated $\underline{\underline{MR}}_D$ (according to Auwers) 27.07; calculated $\underline{\underline{MR}}_D$ (nitrogen increment 2.84) 26.01.

Found %: N 14.43; 14.30
C_5H_7ON. Calculated %: N 14.41.

Ethylisoxazole is a colorless oil with an odor reminiscent of pyridine. It may be preserved a long time without change. After treating 0.931 g of the substance as described under Section III, 0.682 g of precipitate was obtained, corresponding to an α-isomer content of 59.7%.

V. Propylisoxazole

Propyl β-chlorovinyl ketone (9.6 g) was added to a solution of 6.0 g of hydroxylamine hydrochloride in 70 ml of methanol, and the mixture was heated on the water-bath for 3 hours. To this, on cooling, four times its volume of water was added, and the oil that separated was extracted several times with ether. The extract was dried over magnesium sulfate, the ether was driven off, and the residue was vacuum-distilled. Yield 5.8 g (73% of theoretical). After repeated distillation, the substance had the following constants: b.p. 160-161°; 69-70°, 35 mm; d_4^{20} 0.9722; n_D^{20} 1.4468; found $\underline{\underline{MR}}_D$ 30.26; for $C_6H_9ON\ulcorner$ calculated $\underline{\underline{MR}}_D$ (according to Auwers) 31.69; calculated $\underline{\underline{MR}}_D$ (nitrogen increment 2.84) 30.63.

Found %: 12.39; 12.35
C_6H_9ON. Calculated %: N 12.60

Propylisoxazole is a colorless oil with a characteristic odor; it is insoluble in water. It slowly darkens on keeping. After treating 2.059 g of the substance with sodium ethoxide, as indicated in Section III, 1.656 g of precipitate is obtained, corresponding to an α-isomer content of 67.2%.

VI. Isobutylisoxazole

This was prepared and isolated as indicated in Section V from 5.0 g of hydroxylamine hydrochloride and 10.0 g of isobutyl β-chlorovinyl ketone in 100 ml. of methanol. Yield 6.0 g (70% of theoretical). After redistilling, the isobutylisoxazole had the following constants: b.p. 168-169°; d_4^{20} 0.9450; n_D^{20} 1.4480; found $\underline{MR}_D$ 35.46; for $C_7H_{11}ON|^{=}$ calculated $\underline{MR}_D$ (according to Auwers) 36.31; calculated $\underline{MR}_D$ (nitrogen increment 2.84) 35.25.

Found %: N 11.46, 11.34
$C_7H_{11}ON$. Calculated %: N 11.19

Isobutylisoxazole is a colorless oil with a characteristic odor. It is insoluble in water. It slowly darkens on keeping.

VII. 3-Chloromethylisoxazole

This was prepared and isolated as indicated in Section V from 11.0 g of hydroxylamine hydrochloride and 19.4 g of chloromethyl β-chlorovinyl ketone in 100 ml of methanol. Yield 13.8 g (85% of theoretical). After redistilling, the substance had the following constants: b.p. 65-66° at 20 mm; 49-50° at 7 mm; d_4^{20} 1.2745; n_D^{20} 1.4810; found $\underline{MR}_D$ 26.28; C_4H_4ONCl: calculated $\underline{MR}_D$ (according to Auwers) 27.32; calculated $\underline{MR}_D$ (nitrogen increment 2.84) 26.26.

Found %: N 11.72
C_4H_4ONCl. Calculated %: N 11.91

Chloromethylisoxazole is a colorless oil, insoluble in water. It possesses lachrymatory properties. On treating the substance with sodium ethoxide, a precipitate was obtained only after 24 hours, and this consisted entirely of sodium chloride.

VIII. 3-Bromomethylisoxazole

3-Chloromethylisoxazole (5.2 g) was added dropwise with energetic stirring to a hot solution of sodium bromide (10.0 g) in aqueous methanol, and the mixture was boiled for 2 hours. The precipitate of sodium chloride was filtered off, acetone was added to the filtrate until it clouded, and the mixture was warmed for a further 1 hour. The mixture, after cooling, was diluted with four times its volume of water, the oil that separated was extracted with ether, the extract was dried over magnesium sulfate, the ether was driven off, and the residue was vacuum-distilled. Yield 5.1 g (71% of theoretical). After redistilling the substance has the following constants: b.p. 58-60° at 7 mm; n_D^{20} 1.4878.

Found %: N 8.72; 8.67
C_4H_4ONBr. Calculated %: N 8.58

Bromomethylisoxazole is a colorless heavy oil with a sharp odor and lachrymatory effect; it is fairly stable.

IX. 3-Iodomethylisoxazole

3-Chloromethylisoxazole (5.1 g) was added to a solution of 11.0 g of sodium iodide in 40 ml of dry acetone, and the reaction mixture was allowed to stand in the dark for 4 hours. The precipitate of sodium chloride was filtered off (weight 2.38 g; according to theory: 2.59 g), and the filtrate was diluted with three times its volume of water. The heavy oil that came out was separated, washed with a thiosulfate solution, and dried over calcium chloride in the dark. Yield of crude product 8.3 g (92% of theoretical). For purification purposes, the substance may be distilled only in small portions; it then has the following constants: b.p. 96-100° at 1-2 mm; n_D^{20} 1.5700.

Found %: N 7.17
C_4H_4ONI. Calculated %: N 6.60

Iodomethylisoxazole is a heavy oil with a sharp odor; it rapidly darkens o storing.

X. 3-Isoxazole-acetonitrile

3-Chloromethylisoxazole (9.0 g) in 30 ml of alcohol was added to a hot solution of sodium cyanide (12.0 g) in 5 ml of water, and the mixture was heated on the water bath for 2 hours. The mixture, after cooling, was diluted with three times its volume of water and repeatedly extracted with ether. The extract was dried over magnesium sulfate, the ether was driven off, and the residue was vacuum-distilled. Yield 2.8 g (34% of theoretical). After repeated distillation, the substance had the following constants: b.p. 91-92° at 4 mm; d_4^{20} 1.2095; n_D^{20} 1.4751.

Found %: N 26.20

$C_5H_4ON_2$. Calculated %: N 25.94

3-Isoxazole-acetonitrile is a colorless liquid of characteristic odor. It rapidly darkens on keeping.

SUMMARY

1. Alkylisoxazoles are prepared by the reaction of β-chlorovinyl ketones with hydroxylamine. This reaction can be used as a preparative method for synthesizing isoxazoles.

2. It is shown that the substances obtained are mixtures of the isomeric α- and γ-alkylisoxazoles.

3. It is shown that the chlorine atom in 3-chloromethylisoxazole is very readily replaced and may be exchanged for bromine, iodine, and the cyanide group.

M.V.Lomonosov State University
Moscow

Received May 22, 1951

LITERATURE CITED

[1] A.N.Nesmeyanov and N.K.Kochetkov. Proc.Acad.Sci.USSR, 77, 65 (1951).

[2] A.N.Nesmeyanov, N.K.Kochetkov, and M.I. Rybinskaya. Bull.Acad.Sci. USSR. Div.Chem.Sci., 4, 350 (1940).

[3] P. Vigueir. Ann.chim. (8), 28, 488 (1912).

[4] L. Claisen. Ber., 36, 3673 (1903).

[5] L. Claisen. Ber. 42, 59 (1909).

[6] A.N.Nesmeyanov, N.K.Kochetkov, and M.I.Rybinskaya. Bull.Acad.Sci.USSR, Div.Chem.Sci., 4, 395 (1951).

[7] I. Catch, D.Elliot, D.Hey, E.Jones. J.Chem.Soc. 278 (1948).

[8] K.Auwers. Ber., 57, 461 (1924).

[9] A.Ya.Yakubovich and E.N.Merkulova. J.Gen.Chem., 16, 55 (1946).

[10] R. Haltzwart. J.prak.Chem., (2), 39, 238 (1889).

SYNTHESIS OF AROMATIC ORGANO-ANTIMONY COMPOUNDS BY THE AID OF ARYLAZOFORMATES

O. A. Reutov and O. A. Ptitsyna

A method has been developed by one of us in conjunction with A.N.Nesmeyanov for the synthesis of aromatic organo-mercury compounds by the reaction of potassium arylazoformates with mercuric chloride in acetone medium [1]:

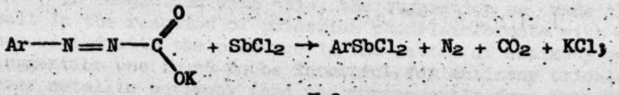
$$ArN_2CO_2K + HgCl_2 \rightarrow ArHgCl + N_2 + CO_2 + KCl$$

In the present work, this method is extended to the synthesis of organo-antimony compounds.

It was found that arylazoformates react readily with antimony trichloride in the cold, both in ethyl acetate and in acetone, giving the corresponding organo-antimony compounds. These were formed, for example, by the reaction of antimony trichloride with the potassium salts of phenylazoformic, p-tolylazoformic, p-bromophenylazoformic, p-nitrophenylazoformic, and β-naphthylazoformic acids. In the reaction of potassium 2,4,6-tribromophenylazoformate with antimony trichloride only 1,3,5-tribromobenzene is formed, and the monopotassium salt of p-sulfophenylazoformic acid does not react at all with antimony trichloride. The separation of the organo-antimony compounds formed was effected by converting them into the corresponding oxides and arylstibonic acids. The results are given in Table 1.

It will be seen from Table 1 that the total yield of organo-antimony compounds is fairly high. The main reaction products are aromatic stiboso compounds (generally prepared by the decomposition of the double diazonium salts [2]) and arylstibonic acids (generally prepared by the Bart-Schmidt reaction [3]). In certain cases (Experiments 1 and 4) double diazonium salts are formed also.

The formation of aromatic stiboso compounds probably proceeds as follows:



$$Ar{-}N{=}N{-}C(=O)OK + SbCl_2 \rightarrow ArSbCl_2 + N_2 + CO_2 + KCl;$$

$$ArSbCl_2 \xrightarrow{H_2O} ArSbO.$$

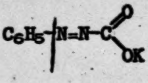
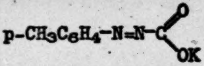
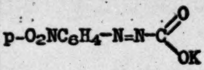
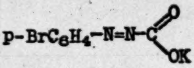
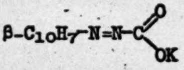
In the formation of arylstibonic acids, as also in the Bart-Schmidt reaction, antimony changes its valency (from three to five). In view of the fact that in several of the reactions we investigated May's salts were isolated, it may be supposed that the formation of arylstibonic acids may proceed through the double diazonium salt stage:

$$ArN_2Cl \cdot SbCl_3 \rightarrow ArSbCl_4 + N_2;$$

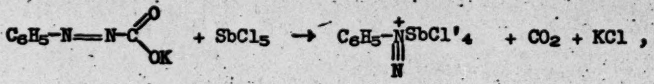
$$ArSbCl_4 \xrightarrow{H_2O} ArSbO(OH)_2.$$

TABLE 1

Reaction of Arylazocarboxylates with Antimony Trichloride

No.	Arylformate	Temperature of reaction (°C)	Amt. of solvent (ethyl acetate), ml	Excess $SbCl_3$ (%)	Reaction products (%)			
					$ArSbO(OH)_2$	$ArSbO$	$(Ar_2Sb)_2O$	Double salt $ArN_2Cl\cdot SbCl_3$
1	 $C_6H_5-N=N-C(=O)OK$	60-70	120	50	-	27	-	16
2	 $p-CH_3C_6H_4-N=N-C(=O)OK$	16-18	120	50	11.5	44	-	-
3	 $p-O_2NC_6H_4-N=N-C(=O)OK$	16-18	120	50	50.7	-	-	-
4	 $p-BrC_6H_4-N=N-C(=O)OK$	16-18	120	50	53.8	-	10.3	18
5	 $\beta-C_{10}H_7-N=N-C(=O)OK$	16-18	120	50	-	90	-	-

The mechanism of the formation of the double diazonium salts[1] was investigated in detail. We found that antimony pentachloride, like the trichloride, reacts energetically in the cold with potassium phenylazoformate according to the equation:



$$C_6H_5-N=N-C(=O)OK + SbCl_5 \rightarrow C_6H_5-\overset{+}{N}(\equiv N)SbCl'_4 + CO_2 + KCl ,$$

giving the double diazonium salt in 76% yield.

In connection with this, the suggestion wa made that the formation of May's salt in the reaction of potassium phenylazoformate with antimony trichloride may be associated with the presence in the latter of antimony pentachloride. However, this suggestion was found to be incorrect, for antimony trichloride that had been distilled over metallic antimony (and was consequently free from $SbCl_5$) gave May's salt in the reaction with $C_6H_5N_2CO_2K$ with the same yield as that given by undistilled $SbCl_3$.

The following scheme:

$$C_6H_5N_2CO_2K \xrightarrow{SbCl_3} C_6H_5N_2COCl \rightarrow C_6H_5N_2Cl + CO$$

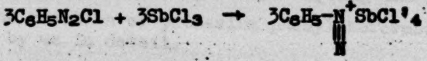
---

[1] It should be noted that in the reaction of potassium arylazoformates with mercuric chloride no double diazonium salts are formed.

was also rejected on the grounds that in the reaction investigated no trace of carbon monoxide is formed.

The further suggestion was made that the formation of double diazonium salts is associated with the reduction of antimony trichloride to compounds of lower valency (in particular, to metallic antimony):

$$3C_6H_5N_2CO_2K + 3SbCl_3 \rightarrow 3C_6H_5N_2CO_2SbCl_2 + 3KCl\ ;$$
$$3C_6H_5N_2CO_2SbCl_2 \rightarrow 3C_6H_5N_2Cl + 3CO_2 + SbCl_3 + 2Sb\ ;$$



$$3C_6H_5N_2Cl + 3SbCl_3 \rightarrow 3C_6H_5-\underset{\underset{N}{|||}}{\overset{+}{N}}SbCl'_4$$

However, such a mechanism is contradicted by the non-formation of metallic antimony in the reactions investigated.

In further investigations it was remarked that the oxygen of the air takes part in the process of the formation of the double diazonium salt. Thus, if immediately after setting on the reaction of ArN_2CO_2K with $SbCl_3$ the reaction mixture is isolated from the air, then the double diazonium salt is not formed even after many days. In control experiments, in which air is not excluded, the double diazonium salt is formed in the course of a few hours. If the reaction mixture that has been preserved for a long time out of contact with the air (and therefore does not contain any double diazonium salt) is brought into the air in an open vessel, then in a few hours $ArN_2Cl \cdot SbCl_3$ is formed. If finally, the reaction of ArN_2CO_2K with $SbCl_3$ is carried out in ethyl acetate at low temperature[1] with simultaneous passage of air, then the double diazonium salt crystallizes straight out of solution.

On the basis of the facts given above we came to the conclusion that the reaction leading to the formation of $ArN_2Cl \cdot SbCl_3$ is as follows:

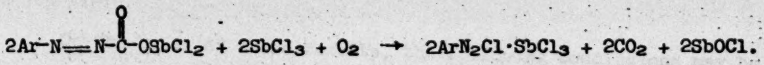
1. $Ar-N{=}N-COOK + SbCl_3 \rightarrow Ar-N{=}N-COOSbCl_2 + KCl.$

The compound formed is only partially decomposed at an early stage of the reaction according to the equation:

$$ArN_2CO_2SbCl_2 \rightarrow ArSbCl_2 + N_2 + CO_2.$$

This is confirmed by the observation that at the beginning not more than half of the theoretical amounts of CO_2 and N_2 is evolved.

2. The remaining part of the substance $ArN_2CO_2SbCl_2$[2] decomposes on standing, only in presence of the oxygen of the air, giving the double diazonium salt:



$$2Ar-N{=}N-\overset{\overset{O}{\|}}{C}-OSbCl_2 + 2SbCl_3 + O_2 \rightarrow 2ArN_2Cl \cdot SbCl_3 + 2CO_2 + 2SbOCl.$$

It should be noted that among the products isolated in the reaction of $C_6H_5N_2CO_2K$ with $SbCl_3$ in acetone and in ethyl acetate was the double salt of benzenediazonium chloride not with $SbCl_3$, but with Sb_2O_3. This "anomalous double salt" is decomposed, like the normal May's salt, with Zn and Cu powder. In the reaction in toluene, only the normal double salt is formed.

---

[1] A low temperature was used in order to slow down the reaction between potassium arylazoformate and antimony trichloride.

[2] It is possible that the variable stability of the $C_6H_5N_2CO_2SbCl_2$ molecules is associated with cis-trans isomerism.

The "anomalous double salt" is evidently formed as a result of the hydrolysis of the normal double salt by the moisture of the air during the evaporation of the solvent (and in certain cases — during the treatment of the reaction products with 5 N hydrochloric acid.

This supposition is confirmed by the formation of $C_6H_5N_2Cl \cdot Sb_2O_3$ from a known specimen of $C_6H_5N_2Cl \cdot SbCl_3$ on hydrolyzing the latter substance in acetone solution.

The reaction of potassium phenylazoformate with antimonytrichloride was studied by us in detail.

The experimental results are given in Table 2

TABLE 2

Reaction between Potassium Phenylazoformate and Antimony Trichloride under Various Conditions

No.	Solvent	Temperature, °C		Solvent (ml)	Excess $SbCl_3$ %	Reaction products, %			
		of reaction	at which solvent distills off			$(C_6H_5)_2SbO_2H$	C_6H_5SbO	$[(C_6H_5)_2Sb]_2O$	Double diazonium salt
1	$CH_3CO_2C_2H_5$	16-18	30-35	120	50	13.1	-	-	-
2	$CH_3CO_2C_2H_5$	60-70	30-35	120	50	26.3	-	-	-
3	CH_3COCH_3	16-18	16-18	120	50	32	-	-	15,3
4	CH_3COCH_3	50	16-18	120	100	20.3	-	-	20
5	$CH_3C_6H_5$	16-18	16-18	120	50	-	-	-	10
6	$CH_3C_6H_5$	16-18	16-18	120	200	-	-	-	45
7	CH_3COCH_3	16-18	16-18	120	200	9	-	-	45
8	CH_3NO_2	16-18	35-40	60	50	9	-	-	-
9	Petroleum ether	50-60	16-18	200	50	-	-	-	10
10	$CH_3CO_2C_2H_5$	60-70	16-18	200	50	-	27	-	16

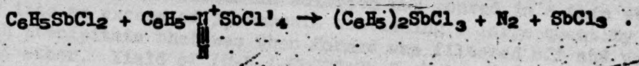
On the basis of these results, the following conclusions may be made:

1. The optimum conditions for the preparation of diphenylstibinic acid consist in the use of acetone as solvent, the carrying out of the reaction at room temperature, and the use of 50% excess of antimony trichloride (expt. 3).

2. Acetone and ethyl acetate are the most suitable solvent for use in the preparation of diphenylstibinic acid.

3. The greatest yield of double diazonium salt is obtained by using a twofold excess of antimony trichloride.

The only difference in conditions between expt. 2 and expt. 10 is that in the first case the solvent is driven off at 30-35°, whereas in the second case it is evaporated off at room temperature. Nevertheless, the reaction products in these experiments are different. This circumstance led us to the idea that chlorodiphenylstibinedichloride may be formed as a result of reaction between dichlorophenylstibine and May's salt, which may occur on heating during the removal of solvent:

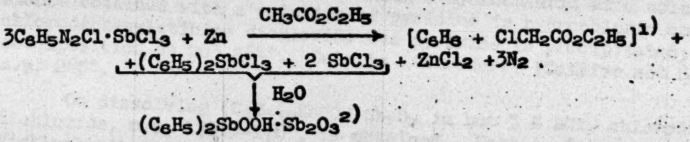


$$C_6H_5SbCl_2 + C_6H_5-\underset{\overset{|||}{N}}{N^+}SbCl'_4 \rightarrow (C_6H_5)_2SbCl_3 + N_2 + SbCl_3 \ .$$

If this supposition is correct, then addition of May's salt to the reaction mixture of expt. 10, followed by heating to 30-35° should raise the yield of diphenylstibinic acid. Experiment confirmed our supposition: the yield of diphenylstibinic acid rose from 26.3 to 37.5%. We performed also a direct proof of the formation of chlorodiphenylstibine dichloride in the reaction of $C_6H_5SbCl_2$ with $C_6H_5N_2^+SbCl_4^-$.

May's salt was first decomposed by zinc dust under the conditions used in the method for the synthesis of organo-antimony compounds by way of double diazonium salts [2]. The inorganic precipitate was filtered off, and to the filtrate, warmed to 50-60°, May's salt was again added. When gas evolution had stopped, the mixture was warmed for some time at 30-35°. In this case the only reaction product was diphenylstibinic acid.

The reaction can be expressed by the scheme:



$$3C_6H_5N_2Cl\cdot SbCl_3 + Zn \xrightarrow{CH_3CO_2C_2H_5} [C_6H_6 + ClCH_2CO_2C_2H_5]^{1)} + \underbrace{+(C_6H_5)_2SbCl_3 + 2\ SbCl_3}_{\downarrow H_2O \atop (C_6H_5)_2SbOOH\cdot Sb_2O_3{}^{2)}} + ZnCl_2 + 3N_2 \ .$$

We have therefore succeeded in directing the decomposition of the double diazonium salt so that, instead of a mixture of products, a single substance $(C_6H_5)_2SbOOH\cdot Sb_2O_3$ is formed, this substance being, at the same time, one that is not formed at all by the diazo method. This method of preparing diphenylstibinic acid is the most suitable preparative synthesis for this substance. In the reaction of $C_6H_5N_2CO_2K$ with $SbCl_3$ in acetone, diphenylstibinic acid is again formed, evidently from dichlorophenylstibine and May's salt.

As was shown by Bruker [4], the complex $C_6H_5SbCl_2\cdot C_6H_5N_2Cl$ decomposes spontaneously in acetone. Taking this into consideration, the fact that we isolated diphenylstibinic acid from acetone solution even when carrying out the reaction and treatment of the reaction mixture at room temperature can be understood.

EXPERIMENTAL

1. Reaction between Potassium Phenylazoformate and Antimony Trichloride in Ethyl Acetate

Potassium phenylazoformate (10 g) (preparation, see [5] and [6]) was sprinkled with stirring into a solution of 17.7 g of antimony trichloride

---

[1]) The products indicated by the square brackets were not identified.

[2]) In the synthesis of diphenylstibinic acid, both by way of arylazoformates and by way of double diazonium salts, it was obtained in the form of a complex with antimony oxide $(C_6H_5)_2SbOOH\cdot Sb_2O_3$

(50% excess) in 120 ml of ethyl acetate at 60-70°. Stirring was continued for a further 30 min. The inorganic precipitate that came out (8 g) was filtered off and washed with ethyl acetate. The washings were united with the filtrate, and the ethyl acetate was driven off in a vacuum at 30-35°. The viscous mass that remained was washed twice with cold 5 N HCl (30 and 15 ml) to remove inorganic antimony compounds. To the washed residue, five times its volume of 96 alcohol was added. The alcoholic solution was poured in a thin stream with stirring into an excess of 5% ammonia containing a large quantity of ice. The yellowish precipitate that was then formed was filtered off and washed with alcohol and ether. Yield of $(C_6H_5)_2SbOOH \cdot Sb_2O_3$ 4.1 g (26.3% of theoretical).

Analysis for antimony in this and all following experiments was carried out by decomposing a weighed amount of the substance with concentrated sulfuric acid and permanganate, decolorizing the mixture obtained with hydrochloric acid, reducing the quinquevalent antimony formed into tervalent by the aid of potassium iodide, and titrating the iodine liberated with 0.1 N sodium thiosulfate [7,8].

Found %: Sb 60.73
$(C_6H_5)_2SbOOH \cdot Sb_2O_3$. Calculated %: Sb 60.85

On passing hydrogen sulfide through a hydrochloric acid solution of the substance obtained, an orange precipitate of antimony sulfide is formed, whereas, under these conditions, a known sample of pure diphenylstibinic acid gives a white precipitate. On mixing a hydrochloric acid solution of the substance obtained with a solution of pyridine in hydrochloric acid, a complex of chlorodiphenylstibine dichloride and pyridine is precipitated; it melts with decomposition at 263-264°. Data in literature: Pfeiffer and Schmidt [8], m.p. 265°.

On dissolving $(C_6H_5)_2SbOOH \cdot Sb_2O_3$ in hot 5 N HCl, chlorodiphenylstibine dichloride, m.p. 175.5-176°, is obtained. Data in literature: Morgan and Micklethwait [9], m.p. 176°; Schmidt [10], m.p. 175°; Bruker [4], m.p. 171-172°.

Found %: C 37.78; H 3.12
$(C_6H_5)_2SbCl_3$. Calculated %: C 37.70; H 2.64

If in the treatment of the reaction mixture ethyl acetate is not driven off, but is caused to evaporate at room temperature, then the "anomalous double salt" (16% of theoretical) and stibosobenzene (27% of theoretical) are obtained.

2. Reaction of Potassium Phenylazoformate with Antimony Trichloride in Acetone

Potassium phenylazoformate (10 g) is sprinkled over a period of 20 min. into a solution of 17.7 g of antimony trichloride (50% excess) in 120 ml of acetone with stirring, which is continued a further 30 min. The inorganic precipitate that forms is filtered off and washed with acetone. The solvent is evaporated off from the filtrate at room temperature. The residual viscous mass is washed twice with 5N HCl. To the washed residue, five times its volume of 96% alcohol is added, and the solution is cooled with snow and salt. A powdery precipitate of violet color is formed. The substance is decomposed by copper powder in acetone; it has no definite melting point.

Found %: Sb 56.40
$C_6H_5N_2Cl \cdot Sb_2O_3$. Calculated %: Sb 56.50

Yield of "anomalous double salt" 3.5 g (15.2% of theoretical). The alcoholic filtrate is poured into an excess of 5% ammonia containing a large amount of ice. The yellow precipitate that forms is washed with alcohol and several times with ether. Yield of $(C_6H_5)_2SbOOH \cdot Sb_2O_3$ 5 g (32% of theoretical).

Found %: Sb 60.56
$(C_6H_5)_2SbO_2H \cdot Sb_2O_3$. Calculated %: Sb 60.85

The substance obtained is converted into chlorodiphenylstibine dichloride, m.p. 174-175°. Data in literature: Schmidt [10], m.p. 175°.

From the ether used for washing $(C_6H_5)_2SbO_2H \cdot Sb_2O_3$, 0.25 g of bis(diphenylantimony) oxide (1.6% of theoretical) was isolated; it was identified in the form of diphenylantimony acetate, m.p. 132°. Data in the literature: Schmidt [10], m.p. 132°; Talalaeva [11], m.p. 133°.

3. Reaction of Potassium Phenylazoformate with Antimony Trichloride in Toluene

Potassium phenylazoformate (4 g) was sprinkled over a period of 20 min. at room temperature into a solution of 15.6 g of antimony trichloride (three-fold excess) in 120 ml of toluene with stirring, which was continued for a further 20 min. The reaction mass thickened up. The precipitate was filtered off, well washed with cold 5 N HCl, and then washed with alcohol. The substance obtained melted at 82-83°, which corresponds to May's salt.

Found %: N 7.46
$C_6H_5N_2SbCl_4$. Calculated %: N 7.60

Yield of May's salt 3.5 g (45% of theoretical). In this experiment no organo-antimony compounds were formed.

4. Reaction of Potassium p-Tolylazoformate with Antimony Trichloride

Potassium p-tolylazoformate (10 g) was sprinkled over a period of 20 min. at room temperature into a solution of 17 g of antimony trichloride (50% excess) in 120 ml of ethyl acetate with stirring, which was continued for a further 30 min. The inorganic precipitate was filtered off (6.5 g), and the filtrate evaporated down at room temperature. The further treatment was as in Experiment 2. 1.7 g (11.5% of theoretical) of p-tolylstibonic acid was separated from alcohol solution in the form of the oxychloride.

Found %: Sb 40.21
$CH_3C_6H_4SbOCl_2$. Calculated %: Sb 40.58

p-$CH_3C_6H_4SbOCl_2$ is a powder, insoluble in organic solvents apart from glacial acetic acid; it forms a complex with pyridine. From ammoniacal solution there was obtained 4.9 g (44% of theoretical) of p-stibosotoluene.

Found %: Sb 53.3
$CH_3C_6H_4SbO$. Calculated %: Sb 53.21

5. Reaction of Potassium p-Nitrophenylazoformate with Antimony Trichloride

Potassium p-nitrophenylazoformate (10 g; preparation, see [12]) was sprinkled over a period of 20 min. at room temperature into a solution of 14.7 g (50% excess) of antimony trichloride in 120 ml of ethyl acetate with stirring, which was continued for a further 30 min. The inorganic precipitate (5.7 g) was filtered off, and the filtrate, after evaporating off the ethyl acetate, was treated as in Experiment 2. From the alcohol solution, a precipitate (2.5 g) that contained no antimony came down (it was not investigated further). On pouring the alcoholic solution into ammonia, 6.8 g (50.7% of theoretical) of p-nitrophenylstibonic acid was obtained;

Found %: Sb 38.98
$O_2NC_6H_4SbO_3H_2$. Calculated %: Sb 39.01

6. Reaction of Potassium p-Bromophenylazoformate with Antimony Trichloride

Potassium p-bromophenylazoformate (5.3 g; preparation, see [12]) was sprinkled over a period of 15 min. at room temperature into a solution of 7.4 g of antimony trichloride (50% excess) in 120 ml of ethyl acetate with stirring, which was continued for a further 30 min. The precipitate formed (2.5 g) was filtered off and washed with ethyl acetate and with cold 5 N HCl. The substance that remained after washing with hydrochloric acid (1.6 g) melted at 112-113° with decomposition; on adding copper powder in acetone, it decomposed with evolution of nitrogen. The substance is a double salt of p-bromobenzenediazonium chloride with $SbCl_3$. Yield 1.6 g (18% of theoretical). Data in literature: Nesmeyanov [13], m.p. 113°.

The ethyl acetate filtrate was treated as in Experiment 2. A precipitate was obtained from alcohol (0.85 g), which was decomposed by copper powder in acetone, but did not have the melting point characteristic for the double salt of p-bromobenzenediazonium salt with $SbCl_3$ (it was not investigated further). On pouring the alcoholic solution into ammonia, 3.5 g of p-bromophenylstibonic acid (53.8% of theoretical) was obtained.

Found %: Sb 36.48
$BrC_6H_4SbO(OH)_2$. Calculated %: Sb 36.59

From the ethereal solution obtained from washing the precipitate produced by ammonia with ether, bis[bis(p-bromophenyl)]antimony oxide was isolated; it was identified in the form of bis(p-bromophenyl)antimony acetate; m.p. 131-132°. Data in the literature: Nesmeyanov [13], m.p. 131-132°; Blicke [14], m.p. 132°.

7. Reaction of Potassium β-Naphthylazoformate with Antimony Trichloride

In the reaction of potassium β-naphthylazoformate (obtained by hydrolysis of the ethyl ester of β-naphthylazoformic acid) with antimony trichloride under the conditions of the previous experiment, β-stibosonaphthalene is formed with a 90% yield. The substance becomes rapidly disproportionated so that, even after reprecipitation, analysis does not give satisfactory results.

Found %: Sb 48.17
$C_{10}H_7SbO$. Calculated %: Sb 46.06

8. Reaction of Potassium Phenylazoformate with Antimony Pentachloride

Potassium phenylazoformate (4 g) is sprinkled at room temperature with stirring into a solution of 7.8 g of antimony pentachloride (25% excess) in 125 ml of toluene. The reaction mixture becomes thick. The precipitate is filtered off and washed with toluene, cold 5 N HCl, and alcohol. The May's salt produced melts at 82-83°. Known May's salt melts at 82-83°, and a mixed test shows no depression. Yield 6 g (76% of theoretical).

9. Reaction of Potassium Phenylazoformate with a Three-Fold Excess of Antimony Trichloride in Acetone

3.5 g of potassium phenylazoformate, reacted under the usual conditions with 12.6 g of antimony trichloride in 125 ml of acetone yielded 3 g of May's salt (45% of theory) and 0.5 g $(C_6H_5)_2SbOOH \cdot Sb_2O_3$ (9% of theory).

10. Reaction of Potassium Phenylazoformate with Antimony Trichloride with Addition of May's Salt

Potassium phenylazoformate (5 g) is sprinkled with stirring into a solution of 8.8 g of antimony trichloride (50% excess) in 120 ml of ethyl acetate at 60-70°. May's salt (12 g) is then added, and the reaction mixture is warmed on the water-bath at 35-40° for 40 min. The inorganic precipitate and the unchanged May's salt are filtered off. The filtrate is treated as in Experiment 2. No precipitate is obtained from alcohol. On pouring the alcoholic solution into ammonia, the complex $(C_6H_5)_2SbOOH \cdot Sb_2O_3$ is obtained. Weight, 2.9 g (37.5% of theoretical).

Found %: Sb 60.77

$(C_6H_5)_2SbO_2H \cdot Sb_2O_3$. Calculated %: Sb 60.85

11. Preparation of the Double Salt of Benzenediazonium Chloride and Antimony Oxide ("Anomalous" Double Salt)

Authentic May's salt (0.5 g) is dissolved in 50 ml of acetone, and water (3 ml) is added to the solution. A white powdery precipitate is formed, which is decomposed by copper powder in acetone, but does not melt on heating up to 185° (authentic May's salt melts at 82-83°).

12. Preparation of Diphenylstibinic Acid by the Double Diazonium Salt Method

May's salt (10 g) is decomposed by 2.5 g of zinc dust in 50 ml of ethyl acetate, previously heated to 60°. The inorganic precipitate is filtered off, and to the filtrate, heated to 60°, May's salt (5 g) is added. There is a vigorous reaction; all the May's salt dissolves in 10-15 min. The solution is heated for 30 min. at 30-35° on a water-bath. The solvent is evaporated off, and the further treatment is carried out as in Experiment 2. May's salt precipitates from alcohol (2.2 g). From ammonia, the complex of diphenylstibinic acid with antimony trioxide is separated (4.2 g, 60.4% of theoretical).

Found %: Sb 60.46

$(C_6H_5)_2SbO_2H \cdot Sb_2O_3$. Calculated %: Sb 60.85

Received June 15, 1951

SUMMARY

1. A method has been developed for the synthesis of aromatic organo-antimony compounds by way of arylazoformates.

2. A mechanism has been proposed for the reactions considered.

3. It has been found that, under the action of antimony tri- or pentachloride, arylazoformates may be converted into aromatic diazonium salts.

4. A convenient preparative method is proposed for the production of diphenylstibinic acids, which are not readily accessible; it consists in the decomposition of the double salt of benzenediazonium chloride and antimony trichloride by means of zinc.

Received June 15, 1851

LITERATURE CITED

[1] A.N.Nesmeyanov and O.A.Reutov. Bull.Acad.Sci.USSR, Div.Chem.Sci., 4, 316 (1948).

[2] A.N.Nesmeyanov and K.A.Kocheshkov. Ibid., 6, 416 (1944).

[3] H. Bart. German patent 250264; H.Schmidt. Ann., 421, 144 (1920); German patent 254421; H.Bart. Ann., 429, 55 (1922).

[4] A.V.Bruker. J.Gen.Chem., 6, 1823 (1936).

[5] A.N.Nesmeyanov and O.A.Reutov. Sci.Mem.Moscow State Univ., 132, 125 (1950).

[6] I.Thiele. Ber., 28, 2600 (1896).

[7] Macallum, J.Soc.Chem.Ind., 42, 468T (1923); K.A.Kocheshkov and A.P. Skoldinov. Synthetic Methods in the Field of the Organometallic Compounds of Antimony and Bismuth. Acad.Sci.USSR, 1947, p.123.

[8] P.Pfeiffer and P.Schmidt. J.prak.Chem., 152, 27 (1939).

[9] G.Morgan and F.Micklethwait. J.Am.Chem.Soc., 99, 2293 (1911).

[10] H.Schmidt. Ann., 429, 138 (1922).

[11] T.V.Talalaeva. Degree thesis. Moscow 1941.

[12] A.Hantzsch and O.Schultze. Ber., 28, 2077 (1895).

[13] A.N.Nesmeyanov. J.Russ.Phys.Chem.Soc., 61, 1393, 1407 (1929).

[14] F.Blicke and U.Oakdale. J.Am.Chem.Soc., 55, 1200 (1933).

INVESTIGATIONS RELATING TO β-AMINO ACIDS

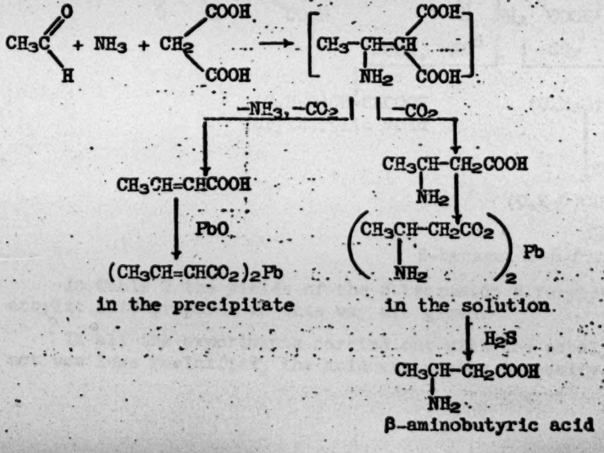
SYNTHESIS AND REACTIONS OF β-AMINOBUTYRIC ACID

V. M. Rodionov and N. G. Yartseva

Although β-aminobutyric acid has been known for a long time [1,2] and many investigators have prepared both the acid, and also a number of its derivatives [3,8] information concerning its reactions is nevertheless still rather scanty. At the same time, this acid is undoubtedly worthy of attention and of thorough comprehensive study as a substance of high physiological activity. As early as 1899 there are indications in the literature that this acid has an effect on the activity of the heart and on the breathing [9,10].

Experiments carried out at our request by Shchepkin, for which we express here our deep gratitude, fully confirmed the earlier observations and clearly showed that, on injection under the skin of a dog, a 0.1% solution of β-aminobutyric acid produces a great increase in blood pressure and an appreciable increase in pulse rate and a more concentrated solution (1%) rapidly produces complete stoppage of the action of the heart. It is very probable that further study of the reactions of β-aminobutyric acid may lead to the discovery of new physiologically active preparations and, possibly, of new medicinal preparations.

The absence of a readily accessible method of preparing β-aminobutyric acid was doubtless one of the obstacles in the way of the study of its reactions. In our investigations, we have used a method developed some time ago in our laboratory for the preparation of this acid [11-14], and we carried out the synthesis according to the scheme below, the β-amino acid required being separated from the reaction mixture by way of the lead salt:


CH₃C(=O)H + NH₃ + CH₂(COOH)₂ → [CH₃-CH(NH₂)-CH(COOH)₂]
-NH₃, -CO₂
-CO₂
CH₃CH=CHCOOH
PbO
(CH₃CH=CHCO₂)₂Pb
in the precipitate
CH₃CH(NH₂)-CH₂COOH
(CH₃CH(NH₂)-CH₂CO₂)₂Pb
in the solution
H₂S
CH₃CH(NH₂)-CH₂COOH
β-aminobutyric acid

However, owing to the very high solubility of β-aminobutyric acid in water (1 g in 1 g of water) and also owing to the high volatility and great tendency to polymerization of the original acetaldehyde, we did not succeed in obtaining yields of greater than 23%. The original method was therefore modified in the following way: 1) instead of introducing a mixture of acetaldehyde and ammonia into the condensation reaction with malonic acid, previously prepared aldehyde-ammonia was used; 2) the reaction was carried out in the presence of a catalyst (trimethylphenylammonium hydroxide); and 3) the condensation product was converted directly into the less soluble benzoyl derivative, without prior separation of the amino acid in the pure state. In this way, the yield was increased to 36% (Table 1).

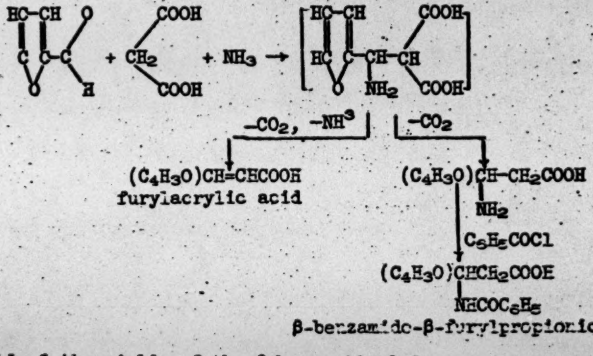
TABLE 1

Experiment No.	Yield (%)	
	With catalyst	Parallel experiment without catalyst
1	17	–
2	17.97	–
3	22.5	14.4
4	18.73	13.7
5	26.7	–
6	36.4	–
7	34.8	14.26
8	36.1	–
9	–	15.01 (with sodium ethoxide)

TABLE 2

Experiment No.	Yields of β-benzamido-β-furylpropionic acid (%)		Yield of furylacrylic acid (%)	
	With catalyst	Without catalyst	With catalyst	Without catalyst
1	11.48	–	6.2	–
2	–	7.4	–	
3	13.4	–	41.8	
4	9,4	5.3	34.8	

As our catalyst always contains a certain amount of sodium ethoxide, one experiment was carried out with ethoxide, but without catalyst; the yield was considerably less. In order to confirm the effect of the catalyst, four experiments were carried out in an analogous way with furfuraldehyde:


HC–CH
C C–C
O H
+ CH2
COOH
COOH
+ NH3 →
HC–CH
HC C–CH–CH
O NH2
COOH
COOH
–CO2, –NH3
–CO2
(C4H3O)CH=CHCOOH
furylacrylic acid
(C4H3O)CH–CH2COOH
NH2
C6H5COCl
(C4H3O)CHCH2COOH
NHCOC6H5
β-benzamido-β-furylpropionic acid

In Table 2 the yields of the β-benzamido-β-furylpropionic acid and furylacrylic acid prepared in this way are given.

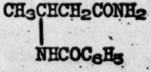
In all the experiments carried out with the catalyst, the condensation product was less resinified, the acid was easier to purify, and the yield was greater.

The suggestion that β-aminobutyric acid could be obtained by the hydrolysis of the benzoyl derivative was not found to be feasible. The benzoyl group does not split off on boiling for 6 hours with 20% HCl, with 10% KOH, or with glacial acetic acid containing HCl. β-Aminobutyric acid prepared through the lead salt is very hygroscopic; it melts with decomposition at 186-187°. Determination of melting point is not reliable as a criterion of its purity owing to the abovementioned hygroscopicity and decomposition on heating. This is the explanation of the various melting points cited by different investigators; 156° – Curtius and Himler; 187-188° – Fischer and Scheibler; 193-194° – Heilbron.

In order to verify our product we prepared the following derivatives of β-aminobutyric acid; methyldihydrouracil [15], the benzoyl derivative (by Schotten-Baumann, yield 38.7%), and the copper salt. Determination of the water of crystallization in the copper salt confirmed the observation of Krebsbakh [16] that it contains two molecules of water of crystallization, and not four, as found by Engel [17].

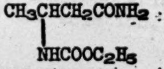
The benzoyl derivative obtained as indicated above by the direct benzoylation of the product of the condensation of acetaldehyde-ammonia with malonic acid melted at 153-154° (according to literature, 155-155.5° [15]), and a mixed test with a sample prepared by the benzoylation of pure β-aminobutyric acid showed no depression of melting point. The solubility of the benzoyl derivative was found to be 0.2459 g per 100 g of water at 25° (according to the literature, 0.2467 [16]). In all the preparations of N-benzoyl-β-aminobutyric acid, also some crotonic acid was isolated in low yield (about 8%).

Apart from the benzoyl derivative, also carbethoxy-β-aminobutyric acid was prepared. The N-benzoyl and N-carbethoxy derivatives were converted by means of thionyl chloride into the corresponding acid chlorides, which gave, on treatment with ammonia, the amides of N-benzoyl- and of N-carbethoxy-β-aminobutyric acid;



$$\underset{\mathrm{NHCOC_6H_5}}{\mathrm{CH_3CHCH_2CONH_2}}$$

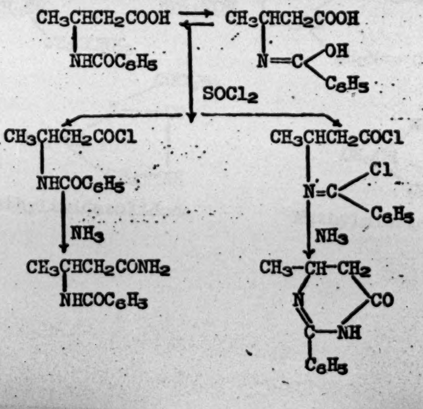
m.p. 199-200°



$$\underset{\mathrm{NHCOOC_2H_5}}{\mathrm{CH_3CHCH_2CONH_2}}$$

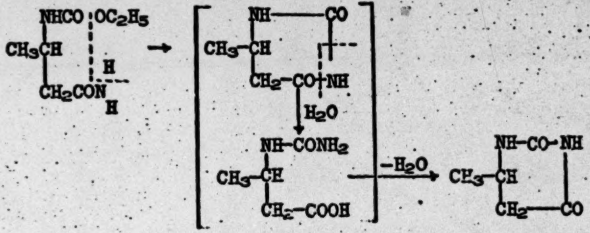
m.p. 138-140°

The reaction went smoothly with the benzoyl derivative, and the yield became constant (82-83%) after three experiments. For the carbethoxy compound, the yield was somewhat less (about 80%). In the preparation of β-benzamidobutyramide, a small amount of 4-methyl-6-oxo-2-phenyltetrahydropyrimidine is always formed;



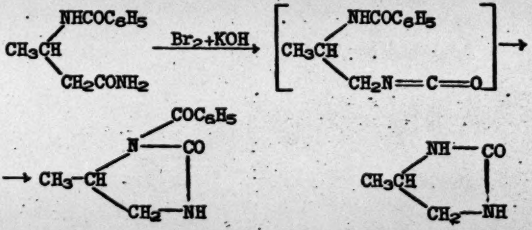
The yield of the pyrimidine depends on the amount of thionyl chloride taken and on the reaction temperature. Using 2 moles of thionyl chloride per mole of the initial amino acid and a temperature of 40-45°, the yield of the pyrimidine did not exceed 20%, while on heating to 80°, the yield was 57%. Using 5 moles of thionyl chloride at 80-82°, the yield rose to 70.6%.

As the work of Rodionov and Zvorykina (18) has shown, the amides of β-alkyl- (or aryl-) β-N-carbethoxyaminopropionic acids may be converted by alkaline hydrolysis into the corresponding β-ureido acids. On alkaline hydrolysis of β-(carbethoxyamino)-butyramide, the product was not the expected β-ureidobutyric acid, but methyldihydrouracil. It is evident that the highly water-soluble β-ureidobutyric acid could not come out of solution, as in the case of other acids, and that, on concentration of the solution, ring-closure occurred with formation of methyldihydrburacil:



The ready ring-closure of β-ureidobutyric acid was observed by us previously in attempts to prepare this acid, following Lippich [19] and Lange and Adickes [20], by boiling β-aminobutyric acid with urea while passing a stream of air to remove ammonia (instead of nitrogen, as proposed by Lippich). Whereas β-aminopelargonic acid and β-phenyl-β-alanine gave the corresponding β-ureido acids under these conditions, β-ureidobutyric acid did not precipitate, and, on subsequent evaporation of the solution, methyldihydrouracil was obtained.

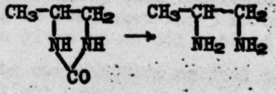
There are already several investigations that show that amides of acylated β-amino acids are converted into derivatives of imidazolidone by reaction with hypobromite [21-24]. By this reaction, β-benzamidobutyramide gave a highly water-soluble and very hygroscopic product, m.p. 86-89°. Analyses of this compound gave reason to suppose that in the reaction with hypobromite a mixture of methylimidazolidone and benzoylmethylimidazolidone is formed:



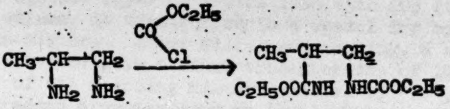
Benzoylmethylimidazolidone Methyimidazolidone

As the work of Zvorykina and Kiseleva has shown that acylimidazolidones (particularly benzoyl derivatives) are readily hydrolyzed, the substance of m.p. 86-89° was hydrolyzed with alkali. Benzoic acid was isolated, and a very hygroscopic substance of m.p. 93.5-95° (unchanged after repeated crystallization from chloroform) was obtained. Its analysis exactly corresponded to methylimidazolidone. Thus, as was to be expected, the amide of an acylated β-aminobutyric acid reacts with hypobromite in the same way as the amides of β-amino acids already investigated in this respect.

The low yield of imidazolidone suggests that under the conditions of the reaction investigated methylimidazolidone is readily hydrolyzed further to 1,2-diaminopropane:



This supposition was fully confirmed, and from the reaction products, with the aid of ethyl chloroformate, the corresponding diurethan was obtained:



EXPERIMENTAL

1. Preparation of β-aminobutyric acid

98% Alcohol (80 ml), acetaldehyde (0.1 mole), malonic acid (0.1 mole), and an alcoholic solution of ammonia (0.11 mole) are mixed with cooling in a 250-ml conical flask. The mixture is warmed under reflux on a water-bath until bubbles of gas are evolved, which generally occurs when the temperature reaches 50-60°. Heating is continued at this temperature until the evolution of gas slows down (about 2 hr). The bath is then brought to the boil, and alcohol with traces of ammonia and aldehyde is driven off. Five hours after the start of the reaction, the water-bath is changed for an oil-bath, and heating is continued at 120° for a further 1 hour.

The reaction product is treated with hot water, transferred to a bowl, and, while stirring and heating over a gauze, PbO is added in small portions (20-25% excess over theoretical). Heating is continued until evolution of NH_3 stops. The precipitate is filtered off under suction and washed several times on the filter with hot water. The filtrate is precipitated, on cooling, with H_2S. After removing PbS, the solution is evaporated on the water-bath to a thick syrup, a few drops of absolute alcohol are added, then some ether and nuclei for crystallization. The mass is left in a desiccator over H_2SO_4, and after two or three days it all crystallizes out. It is stirred with absolute alcohol and sucked off on the funnel, where it is washed with absolute alcohol. The crystals are dried in a dessicator over H_2SO_4. Melting point 176-179°. It is purified by recrystallization from water. Melting point in a sealed capillary 186-187°. Yield did not exceed 23%.

2. Preparation of β-(Benzoylamino)-butyric Acid

a) Aldehyde-ammonia. Prepared according to Gattermann [25].

b) Catalyst (trimethylphenylammonium hydroxide). Prepared as for the preparation of β-alanine [26].

c) β-Benzamidobutyric acid. Malonic acid (10.4 g = 0.1 mole) in 30 ml of 98% alcohol is cooled in a mixture of ice and salt. Aldehyde-ammonia (6.1 g) is mixed with 30 ml of alcohol in a 250-ml conical flask, also with cooling, and the two solutions are mixed together. After stirring for 10-15 min., catalyst (5 ml) is added. The flask is then connected to a reflux condenser, and the reaction mixture is heated on a water bath to 50-60°. After about 2 hours, when the separation of gas bubbles has stopped, the bath is raised to the boil and the alcohol, with the residues of aldehyde and ammonia, is driven off. Heating is continued for 3 hr. on a vigorously boiling bath, and further heating is then given on an oil-bath at 120-130° for 1 hour.

The condensation product is a transparent yellow resin. It is dissolved with slight warming in 40-50 ml of diluted (1:1) HCl and is extracted, after cooling, with ether in order to remove the unsaturated (crotonic) acid.[1]

The aqueous layer is neutralized with KOH (to Congo Red) and, after measuring its volume, is transferred to a vessel for benzoylation, which is placed in a cooling mixture. After mixing and cooling, a solution of 18 g of KOH in sufficient water to give a final concentration of 10-12% is added. When the temperature of the reacting mixture reaches +5 - 10°, benzoyl chloride (14 g = 0.1 mole) is added dropwise over an hour. Stirring is continued under cooling for one hour, and then for a further 2 hr. at room temperature. When benzoylation is complete, the solution is twice extracted with ether to remove residual benzoyl chloride and any benzamide that may be formed; the cooled and stirred solution is then precipitated with strong hydrochloric acid. β-Benzamidobutyric acid comes down in the form of a rapidly crystallizing oil. Next day, the crystals are filtered off under suction, washed on the filter with water, and dried at 70-80°. The dry substance is stirred with absolute ether to remove benzoic acid, filtered, and washed again on the filter with ether. It is recrystallized from water; m.p. 153-154°. Yield 7-8 g, i.e. 30-36% of theoretical.

Found %: C 63.43; 63.44; H 6.38; 6.31; N 6.74; 6.72
$C_{11}H_{13}O_3N$. Calculated %: C 63.76; H 6.28; N 6.76

3. Isolation of Crotonic Acid

Ether extract No. 1, after washing with water, drying over Na_2SO_4, and removal of ether, gave an oil, which distilled over between 167 and 190° and partly crystallized on standing. The thin needle-like crystals were dried on a porous plate; m.p. 71-72°; b.p. 186-189°.

Found %: C 55.22; 55.03; H 7.12; 7.21
$C_4H_6O_2$. Calculated %: C 55.81; H 6.97

The filtrate from the crystals was fractionated once again. The main fraction came over between 169 and 182°; n^{14} 1.4439. In none of the experiments did the yield of crotonic acid exceed 8%. In order to convert the cis- into the trans-form, the liquid form was heated for 2 hr. at 180° and then distilled. The main fraction came over at 185-188°. The distillate crystallized out; m.p. 70-72°.

4. Preparation of β-Benzamidofurylpropionic Acid

Furfuraldehyde (10 g) is mixed with cooling with 50 ml of absolute ether in a 250-ml flask, and the solution is saturated with dry NH_3. As much ether as possible is removed by the aid of a pump, and the residual half-solid mass of aldehyde-ammonia is mixed in the cold with 15 ml of absolute alcohol and with a cooled solution of 10.8 g of malonic acid in 35 ml of absolute alcohol. Catalyst (5 ml) is added, and the mixture is well stirred. After 10-15 min the flask is connected to a reflux condenser, and the mixture is warmed on the water-bath. At 65-70°, evolution of gas commences. This temperature is maintained until the evolution of gas bubbles slows down; the temperature is then raised to 99-100°. The total time of heating is about 5 hr. The reaction product (a dark-colored resin¹⁾) is treated with 100 ml of diluted (1 : 1) hydrochloric acid and is extracted with ether. After treating the ether extract with charcoal and removing the solvent, a brownish-red substance remains; after repeated dissolution in caustic potash and reprecipitation, a white crystalline powder of furylacrylic acid, m.p. 140-141°, is obtained. The hydrochloric acid solution is neutralized with caustic potash and benzoylated by adding first a solution of 18 g of KOH in 80 ml of water (total volume of liquid, 140 ml) with cooling and stirring and then 14 g of benzoyl chloride drop by drop over one hour at +5 to +10°. Stirring continues for 1 hr. further in the cold and for 1 hr. at room temperature. The reaction product is extracted with ether, and the aqueous layer is precipitated with strong hydrochloric acid. A crystalline precipitate of β-benzamidofurylpropionic acid (white in experiments with catalyst, gray without catalyst, is formed. Next day, it is filtered off, washed on the filter with water, dried at 70-80°, and washed with ether to remove contaminating benzoic acid. M.p. after recrystallization from water: 179-180°. The yields are indicated above.

---

[1] Ether extract No. 1.

5. Preparation of β-Benzamidobutyramide and of 4-Methyl-6-oxo-2-phenyltetrahydropyrimidine

β-Benzamidobutyric acid (10 g) is treated at 40-45° with thionyl chloride (2 moles of $SOCl_2$ per mole of acid) until bubbles of gas cease to appear. Residual $SOCl_2$ is removed in a vacuum. The acid chloride obtained is stirred in 500 ml of absolute ether, and, under cooling with ice and salt, a stream of dry NH_3 is passed, up to saturation, through the ethereal suspension. The precipitate is filtered off, washed with hot water, with 10% KOH, and again with water, recrystallized from water, and dried at 70-80°.

M.p. of β-benzamidobutyramide: 199-200°. Yield 8.2-8.34 g, i.e. 82-83% of theoretical.

Found %: C 64.88; 64.70; H 6.76; 6.82; N 13.60; 13.64
$C_{11}H_{14}O_2N_2$. Calculated %: C 64.07; 6.79 N 13.59

After driving off the solvent, light-yellow 4-methyl-6-oxo-2-phenyltetrahydropyrimidine was precipitated from the ethereal filtrate. After recrystallization from benzene it melted at 119-120°. The yields are indicated above.

Found %: N 14.58; 14.26
$C_{11}H_{12}N_2O$. Calculated %: N 14.89

6. Preparation of β-(Carbethoxyamino)-butyramide and Its Hydrolysis with 5% KOH

β-Aminobutyric acid (7 g) was dissolved in 100 ml of 11.5% aqueous KOH (3 moles). Chloroformic ester (8.5 g = 1.1 mole per mole of amino acid) was added with shaking and cooling with ice water, and the mixture was allowed to stand for 24 hr. The solution was then acidified to Congo Red and extracted with ether. The oil that remained after removing the ether crystallized out only after standing for a long time in a desiccator. The purification of the

---

1) In the experiments without catalyst the product is almost black; in experiments with catalyst it is gray.

greasy crystals was very difficult. For this reason, the β-(carbethoxy)-butyric acid, of which 6.7 g was obtained, was converted without further treatment into the amide by the method described above for β-benzamidobutyramide. After recrystallization from benzene the β-(carbethoxyamino)-butyramide melted at 138-140°. Yield (5 g) 87%.

Found %: N 16.51; 16.43
Calculated %: N 16.09

0.5 g of this amide was boiled with 5 ml of KOH for half an hour over a gauze. The solution was acidified with HCl. The expected β-ureidobutyric acid was not precipitated. The mixture was evaporated to dryness and extracted with absolute alcohol. The solution was filtered and evaporated down to a syrup. It was left in a desiccator until it crystallized. The crystals were dried on a porous plate; m.p. 216-218°. A mixed test with a sample of methydihydrourcil, prepared according to E. Fischer and Röder [15], gave no depression on melting.

7. Action of Hypobromite on β-Benzamidobutyramide

Preparation of Methylimidazolidone

Starting substances:

β-Benzamidobutyramide	5.15	g (0.025 mole)
Bromine	8	g (2.35 ml)
KOH	11.2	g
Water	11.5	ml

The bromine is added dropwise to a stirred solution of KOH, cooled to -10°. The amide is then introduced in small portions at a time into the light-yellow hypobromite solution. The temperature in the mixture is 0 to +2°. At first the amide dissolves readily, but towards the end the liquid becomes opaque. After adding all the amide (2-3 hr), the flask containing the reaction mixture is immersed in a water-bath at 80°. As soon as the temperature reaches 40-55°, there is a vigorous evolution of gas, and the solution is decolorized. The flask is immediately taken off the bath, but the temperature of the mixture continues to rise and attains 65-68°. When further immersion of the flask in the 80° bath followed by its removal no longer leads to a jump in temperature, the mixture is heated at 60° for a further 10 min, and then cooled. A precipitate of amide that has not reacted (about 0.4 g) comes down. The filtrate from the removal of the amide is precipitated with hydrochloric acid (1:2). Benzoic acid is precipitated (about 76% of theoretical). As the other products of the reaction are of high solubility in water, the acid filtrate from the benzoic acid has to be evaporated down to dryness. The residue gives a reaction for nitrogen. The dry substance is extracted with chloroform (extract No. 1) and then, with warming, with 99% alcohol (extract No. 2).

Extract No. 1. After drying with Na_2SO_4 and driving off the chloroform, a mass reminiscent of petroleum jelly remained. Under the microscope, it was seen to consist of crystals impregnated with oil. On redissolving in chloroform, a very small amount of unreacted amide (0.1-0.14 g) was obtained; this was filtered off, and the filtrate was dried over Na_2SO_4. The product, after driving off the solvent, was a very hygroscopic, light-yellow substance, which turned into a powder on drying in a desiccator over P_2O_5; m.p. 86-89°. Analysis showed that this was a mixture of methylimidazolidone and benzoylmethylimidazolidone. The amount of benzoic acid obtained also pointed to the incomplete splitting-off of the benzoyl group.

In order to obtain the pure imidazolidone, the substance of m.p. 86-89°

(1.82-1.93 g) was heated for 2 hr on the water bath under reflux with 30 ml of 20% KOH. A reddish oil came out. On acidifying and shaking repeatedly with ether, benzoic acid went over into the ether. After removal of the ether layer, the aqueous solution was evaporated down to dryness, and the dry residue was extracted with chloroform. After drying over Na_2SO_4 and removal of solvent, a substance of m.p. 93-95° was obtained. Its analysis corresponded to methylimidazolidone:

Found %: C 47.81; 48.06; H 8.0; 7.96; N 28.19; 28.15
$C_4H_8ON_2$. Calculated %: C 48.0; H 8.0; N 28.0

Extract No. 2. After driving off the alcohol, a brownish-red thick resinous mass was obtained. In order to remove residual imidazolidone, it was triturated with chloroform; the chloroform was poured off, and the residue was dissolved in 20% KOH. The solution was mixed in the cold with chloroformic ester. After 24 hr, the upper layer of the oil that was formed crystallized out. The crystals were laid out on a porous tile and then purified by repeated dissolution in ether and reprecipitation with petroleum ether. Analysis showed that this was the diurethan of propylenediamine; 1.39 g was obtained, m.p. 69-71°.

Found %: C 49.85; 49.78; H 7.91; 8.05; N 12.34; 12.36
$C_9H_{18}O_4N_2$. Calculated %: C 49.54; H 8.25; N 12.84

As was to be expected, under the conditions of the reaction with hypobromite and of the subsequent treatment, the imidazolidone is hydrolyzed with formation of propylenediamine.

SUMMARY

1. In the condensation of malonic acid with acetaldehyde-ammonia, it was found possible to increase the yield of β-aminobutyric acid, which was isolated in the form of its benzoyl derivative, up to the value of 36%, if a catalyst (trimethylphenylammonium hydroxide) was used.

2. The benzoyl group does not split off from β-benzamidobutyric acid when the latter is boiled for 6 hr with 20% HCl, or with 10% KOH, or with glacial acetic acid containing HCl.

3. As in the case of other β-amino acids studied previously, in the preparation of the amide of β-benzamidobutyric acid there is formed also the corresponding methyloxophenyltetrahydropyrimidine. The yield of the latter depends on the amount of thionyl chloride taken in the reaction of acid chloride formation and on the temperature at which this reaction is carried out.

4. When treated with hypobromite, β-benzamidobutyramide gives methylimidazolidone. Under the conditions of the reaction and of the subsequent treatment, the latter is partially hydrolyzed and is converted into propylenediamine.

D.I. Mendeleev Chemico-Technological Institute. Received July 13, 1951

LITERATURE CITED

[1] Engel. Ber., 21, 523 (1888); Comptes rendues, 106, 1677 (1888).

[2] Balbiano. Gaz.chim.Ital., 10, 139 (1880); Ber., 13, 312 (1880).

[3] Weidel, Roitner. M. 17, 186 (1896).

[4] E. Fischer. Ber., 34, 343, 3751 (1901).

[5] T. Curtius. J. prak. Chem., (2) 70, 209 (1904).

[6] E. Fischer, H. Scheibler. Ann., 383, 337 (1911).

[7] H. Scheibler. Ber., 45, 2278 (1912).

[8] Skita, Wulff. Ann., 453, 206 (1927).

[9] Sienberg. Z. klin. Med., 38, 78 (1899).

[10] K. Morsch. M. 60, 50 (1932).

[11] V.M.Rodionov and E.I.Malevinskaya. Ber. 59, 2952 (1928).

[12] V.M.Rodionov and A.M.Fedorova. Arch. der. Pharm., 1933 p. 287; Ber., 60, 804 (1927).

[13] V.M.Rodionov and V.K.Zvorykina. Bull. Acad. Sci. USSR, Div. Chem. Sci., 3, 216 (1943).

[14] V.M.Rodionov and V.V.Kiseleva. J. Gen. Chem., 18, 1913 (1948).

[15] E. Fischer, Roder. Ber., 34, 3751 (1901).

[16] Krebsbakh. Thesis, Moscow State Univ., Medical Faculty. 1906.

[17] Engel. Bull. Soc. chim. France, 50, 102 (1888).

[18] V.M.Rodionov and V.K.Zvorykina. Proc. Acad. Sci. USSR, 45, No.6, 853 (1949).

[19] F. Lippich. Ber., 41, 2958, 2974 (1908).

[20] K. Lange and F. Adickes. Z. physiol. Chem., 269, 263 (1941).

[21] P. Karrer and A. Schlosser. Helv. Acta, 6, 411 (1932).

[22] S.I.Kanevskaya. J. prak. Chem., (2) 132, 355 (1932).

[23] V.K.Zvorykina. Thesis. Moscow, 1944.

[24] V.M.Rodionov and V.V.Kiseleva. J. Gen. Chem., 18, 1905 (1948).

[25] L. Gattermann and T. Wieland. Laboratory Methods of Organic Chemistry. State Chemical Press, 1948, p. 245.

[26] V.M.Rodionov and N.G.Yartseva. Bull. Acad. Sci. USSR, Div. Chem. Sci., 2, 251 (1948).

SYNTHESIS AND CHARACTERIZATION OF β-(β-NAPHTHYL)-β-AMINOPROPIONIC ACID AND OF CERTAIN OF ITS DERIVATIVES

Communication 1

V. M. Rodionov and B. I. Kurtev

In previous investigations in our laboratory it has been shown that aromatic and aliphatic aldehydes readily react with malonic acid in presence of ammonia. Reaction proceeds mainly in two directions: a β-amino acid is formed, and a derivative of acrylic acid arises in a side-reaction. These reactions are as follows:

$$R(Ar)CHO + NH_3 + CH_2(COOH)_2 \rightarrow R(Ar)CH(NH_2){-}CH_2COOH + H_2O + CO_2 \tag{I}$$

$$R(Ar)CHO + CH_2(COOH)_2 \rightarrow R(Ar)CH{=}CHCOOH + H_2O + CO_2. \tag{II}$$

The total yield of the two readily separable substances is about 80%, 35-50% being β-amino acid. The first attempts to extend this reaction to α-naphthaldehyde led to the conclusion that in this case naphthylacrylic acid is considerably more readily formed, while the yield of β-(α-naphthyl)-β-aminopropionic acid is insignificant [1]. However, it was shown in further experiments that β-naphthaldehyde gives the β-amino acid of this series with a yield of about 60%, and recently Kravchenko [2], by changing to some extent the conditions for the condensation of α-naphthaldehyde with malonic acid, has obtained a record yield of β-(α-naphthyl)-β-alanine (more than 70%).

In order to prepare β-(β-naphthyl)-β-aminopropionic acid, it was necessary to work out a method of preparing β-naphthaldehyde. This compound was first prepared by Batterschall [3] in 1873 by dry distillation of the Ca salts of β-naphthoic and formic acids. A better yield (50%) was obtained by Chichibabin [4] by treating β-naphthylmagnesium bromide with orthoformic ester. By replacing bromonaphthalene by iodonaphthalene, Peter Sah increased the yield of β-naphthaldehyde to 70%[5]. There is a certain preparative significance in the method based on the ω-bromination of β-methylnaphthalene followed by treatment of the bromo-derivative with hexamethylenetetramine [6].

Very good yields (up to 90%) can be obtained also by the use of Stephen's method - reduction of β-naphthonitrile followed by hydrolysis [7]:

$$C_{10}H_7CN \xrightarrow[\text{ether}]{SnCl_2} C_{10}H_7CCl{=}NH \xrightarrow{H_2O} C_{10}H_7CHO.$$

A fairly high yield (about 70-80%) is obtained also by the reduction of β-naphthoyl chloride, following Rosenmund [8]. All these methods, in spite of their high yields, are composed of many stages and give a great deal of difficulty. For this reason, an attempt was made to prepare β-naphthaldehyde by oxidizing β-methylnaphthalene with selenium dioxide. The oxidation of methyl groups in aromatic compounds to aldehyde groups has been employed on a number of occasions with great success [9].

The first experiments on the preparation of β-naphthaldehyde by this method have already been described [9]. The yield of aldehyde was only 34% of theoretical, on the basis of the β-methylnaphthalene taken. We have succeeded in almost doubling the yield of β-naphthaldehyde by using a mixture of naphthalene and methylnaphthalene (1.5:1) in the oxidative reaction. At first the reaction was carried out with mechanical stirring, but it was found later that the reaction could be carried out equally successfully by adding selenium dioxide to the mixture of naphthalene and β-methylnaphthalene heated to 220°. This method of obtaining β-naphthaldehyde, using the readily accessible β-methylnaphthalene, is the most suitable for preparative purposes. The product that we obtained melted at 60.5-61.5° and was used by us for the synthesis of β-(β-naphthyl)-β-aminopropionic acid, of N-(β-naphthal)-methylamine, of β-(β-naphthyl)-acrylic acid and its ester, and of β-naphthalmalonic acid (see Experimental section).

β-(β-Naphthyl)-β-alanine, $C_{10}H_7CH(NH_2)CH_2COOH$, was first prepared by Rodionov's method. The yield (16.5%) was not very high, and variations of the basic method were therefore tried, viz. Johnson's method [10] and the method of Rodionov and Kravchenko [2]. In Johnson's method, ammonium acetate is used instead of alcoholic ammonia, and in Kravchenko's – a mixture of ammonium acetate and glacial acetic acid is used. By the use of Johnson's method, the yield of β-(β-naphthyl)-β-alanine was raised to 65%, and when we used Kravchenko and Rodionov's modification, which appears to be the most suitable for aldehydes of the naphthalene series, the yield rose to 69% of the theoretical.

When Johnson's method was used, the residue remaining after separating the amino acid was not investigated. In the remaining experiments, carried out by Kravchenko's method, the residue appeared to be almost pure β-(β-naphthyl)-acrylic acid. The formation of β-naphthalmalonic acid could not be detected in this method. The results of the experiments are given in Table 1.

TABLE 1

Method of preparation	β-(β-Naphthyl)-β-alanine (%)	β-(β-Naphthyl)-acrylic acid (%)	β-Naphthalmalonic acid (%)
a) Basic method	16	27	17
b) Johnson's method	65	The unsaturated acids were not investigated	
c) Rodionov and Kravchenko's modification	69	19	Not detected
d) In a large amount of glacial acetic acid	58.5	31	Not detected

For the characterization of β-(β-naphthyl)-β-alanine, several derivatives were prepared: 1) the methyl ester, by heating the free β-amino acid with methyl alcohol in presence of sulfuric acid; 2) the amide, by allowing the methyl ester to stand with ammonia at room temperature for a month; 3) N-benzoyl-β-(β-naphthyl)-β-alanine; 4) N-acetyl-β-(β-naphthyl)-β-alanine and its amide and anilide; and 5) N-methyl-β-(β-naphthyl)-β-alanine. The yields and melting points of these substances are given in Table 2.

TABLE 2

Formula and name	Yield (%)	M.p. of pure substance (in °C)
$\beta\text{-}C_{10}H_7CH(NH_2)CH_2COOCH_3$ Methyl ether of β-(β-naphthyl)-β-alanine	87.5	94-95
$\beta\text{-}C_{10}H_7CH(NH_2)CH_2CONH_2$ Amide of β-(β-naphthyl)-β-alanine	64.5	143.5-144.5
$\beta\text{-}C_{10}H_7CH(NH\cdot CO\cdot C_6H_5)CH_2COOH$ N-Benzoyl-β-(β-naphthyl)-β-alanine	90.5	209-210
$\beta\text{-}C_{10}H_7CH(NH\cdot COCH_3)CH_2COOH$ N-Acetyl-β-(β-naphthyl)-β-alanine	77	177.5-178.5
$\beta\text{-}C_{10}H_7CH(NHCOCH_3)CH_2CONH_2$ Amide of N-acetyl-β-(β-naphthyl)-β-alanine	~80%	230-231
$\beta\text{-}C_{10}H_7CH(NH\cdot COCH_3)CH_2CONH\cdot C_6H_5$ Anilide of N-acetyl-β-(β-naphthyl)-β-alanine	-	296-237
$\beta\text{-}C_{10}H_7CH(NHCH_3)CH_2COOH$ N-methyl-β-(β-naphthyl)-β-alanine	49[1] 29.5[2]	195-195.5

[1] Yield from β-naphthaldehyde, malonic acid, and potassium acetate in presence of glacial acetic acid.

[2] Yield from N-(β-naphthal)-methylamine and malonic acid (see Experimental section).

EXPERIMENTAL

β-Naphthaldehyde. A mixture of 56.8 g of β-methylnaphthalene (b.p. 235-236°) and 80 g of naphthalene was heated on an oil-bath up to a temperature of 220°. Freshly activated selenium dioxide (44.4 g) was introduced into the mixture at this temperature in small portions at a time over 30-40 min. After each addition, the mixture was stirred with a glass rod, and vigorous ebullition occurred. Five minutes after adding the last portion of selenium dioxide, the reaction mixture began to boil gently. Heating was discontinued, and the cooled mixture was dissolved in ether and filtered from the black selenium powder. The residue was carefully washed with ether. The main filtrate and the washings were mixed with 150 ml of a bisulfite solution and stirred mechanically for 3 hours. A voluminous precipitate of the bisulfite compound of β-naphthaldehyde began to precipitate rapidly. After a few hours the strongly colored ethereal solution above the precipitate was carefully poured off; ether was again poured on to the precipitate, and the mixture was stirred and allowed to stand until the ether had completely separated. The latter was again poured off, and the precipitate, mixed with a fresh portion of ether, was transferred to a filter and washed on the filter with ether until the washings became completely colorless.

The aldehyde-bisulfite compound obtained in this way - it consisted of fine faintly pink scales - was introduced with stirring into a hot strong soda solution. Naphthaldehyde separated as a dark-colored oil. The whole mass was diluted with cold water and stirred. The naphthaldehyde, which rapidly crystallized, was filtered off, washed with water, and immediately steam-distilled.

The completely colorless crystalline β-naphthaldehyde was filtered off and dried at 50°. Yield 41.3 g, i.e., about 66% of theoretical; m.p. 60.5-61.5°.

N-(β-Naphthal)-methylamine. To a solution of 15.6 g of β-naphthaldehyde and 8.1 g of methylamine hydrochloride in 50 ml of alcohol a solution of 6.2 g of caustic potash in 40 ml of alcohol and 20 ml of water is added drop by drop with stirring and cooling. Crystallization rapidly sets in. After 5-6 hours the crystalline precipitate is filtered off and washed with alcohol and water. Yield 11.4 g (about 67% of theoretical); m.p. 81-82°. From the mother liquor a further 5.2 g of a strongly contaminated product, m.p. 66-74°, may be separated by adding water.

N-(β-Naphthal)-methylamine crystallizes well from gasoline (b.p. 115-135°). Glistening scales; m.p. 80.6-81.6°.

Found %: N 8.28; 8.50
$C_{12}H_{14}N$. Calculated %: N 8.28

N-(β-Naphthal)-methylamine is readily soluble in alcohol, ether, benzene, and CCl_4; it is insoluble in water. It dissolves unchanged in hydrochloric acid in the cold, but is hydrolyzed on heating.

The methyl ester of β-(β-naphthyl)-acrylic acid was prepared by warming naphthylacrylic acid (2 g) in methyl alcohol (20 ml) in presence of sulfuric acid (3 g). Yield about 2 g, i.e. 94% of theoretical, m.p. 93-93.5° (after recrystallization from methyl alcohol). It consists of glistening scales.

Found %: C 79.02; H 5.51
$C_{14}H_{12}O_2$. Calculated %: C 79.25; H 5.70

β-(β-Naphthyl)-β-alanine

a) Preparation by Rodionov's basic method. A mixture of 7.8 g of β-naphthaldehyde, 5.72 g of malonic acid, and 13.4 ml of a 7% solution of ammonia in absolute alcohol was heated in a flask, fitted with condenser for distillation, on the water bath for 10 hours. The dry residue in the flask weighed about 12 g. Half of the residue was ground into a fine powder and was extracted for 1½ hours with 20 ml of hydrochloric acid (1:10) with mechanical stirring. The insoluble residue was filtered off and washed with dilute hydrochloric acid. The acid filtrate was evaporated down somewhat on the water-bath, cooled, extracted with ether several times, and then neutralized with sodium acetate. After standing for 10-12 hours, the precipitate that formed was filtered off, washed with water, with alcohol, and then with ether, and finally dried at 70-80°; m.p. 215-216° with decomposition; yield 0.85 g, i.e, only 16% of theoretical. After recrystallization from methyl alcohol, the melting point was raised to 220-221° (with decomposition).

Found %: C 72.11; 72.08; H 6.05; 5.95; N 6.91, 6.92
$C_{13}H_{13}O_2N$. Calculated %: C 72.54; H 6.09 N 6.51

The residue forms colorless thick plates, almost insoluble in the cold in water, methanol, and ethanol. It does not dissolve in acetone, benzene, or ether, but dissolves well in glacial acetic acid. It remains unchanged after long boiling with caustic soda (10%) or with conc. HCl. Investigation of the residue that is insoluble in hydrochloric acid showed that it consists essentially of β-naphthalmalonic acid (1.02 g isolated) and β-(β-naphthyl)-acrylic acid (1.31 g).

b) Preparation by Johnson's variant. β-Naphthaldehyde (15.6 g), malonic acid (10.4 g), ammonium acetate (10 g), and alcohol (25 ml) were heated for 10-11 hours on a boiling water bath. At first the mixture dissolved rapidly, and then a brisk evolution of gas set in and after 5-6 min. a voluminous precipitate was formed. In order to isolate the β-(β-naphthyl)-β-alanine, dil. HCl (60 ml, 1:5) was added, with constant stirring, to the reaction mixture. After heating for 10 min. at 70-80°, the precipitate formed was filtered off, washed on the filter three times with warm hydrochloric acid (1:5), and then washed with water. The acid filtrate together with the water washings were extracted 5-6 times with ether and neutralized with a solution of sodium acetate. The voluminous precipitate that formed was allowed to stand for some time and then filtered off and washed with water. The crude product was boiled for two hours with 100 ml of alcohol and then filtered hot. The residue on the filter was washed with alcohol and ether and was dried at 70-80°. Yield of β-(β-naphthyl)-β-alanine 14 g, i.e. about 65% of theoretical. The residue that was insoluble in hydrochloric acid was heavily contaminated naphthylacrylic acid and was not investigated in greater detail.

c. Preparation by Rodionov and Kravchenko's variant. β-Naphthaldehyde (6 g), malonic acid (5 g = 25% excess), ammonium acetate (12 g = about 300% excess), and glacial acetic acid (20 ml) were heated on a boiling water-bath for 10 hours. The mixture went into complete solution at 85°, with vigorous gas evolution. Already after boiling for 1 hour a voluminous crystalline precipitate started to separate. When reaction was complete, water (50 ml) was added to the mixture, and the reaction mass was carefully stirred. The well cooled precipitate was filtered off and repeatedly extracted with water. The united aqueous extracts were acidified with hydrochloric acid to Congo Red and were evaporated down almost to dryness on the water bath. The residue was treated in the way indicated above and yielded 0.52 g of β-(β-naphthyl)-β-alanine.

The water-insoluble part of the solid reaction mass was extracted with warm hydrochloric acid; the hydrochloric acid filtrate was extracted several times with ether and then evaporated to dryness on the water bath. 6.81 g of the amino acid hydrochloride (m.p. 210-212° with decomposition) was obtained. One third of the fresh hydrochloride (2.27 g) was converted into free β-amino acid. For this purpose the hydrochloride was dissolved in dilute acid, filtered from a small amount of insoluble precipitate, extracted with ether, and precipitated in the usual way with sodium acetate. After purifying by boiling with alcohol, 1.73 g of very pure β-(β-naphthyl)-β-alanine, m.p. 217-218°, was obtained. Thus, the total yield of the latter was 5.71 g, i.e. 69% of theoretical. The residue that remained after treating the reaction mass with hydrochloric acid was fairly pure β-(β-naphthyl)-acrylic acid, m.p. 206-207°. Yield 1.46 g, i.e. about 19% of theoretical.

d. On carrying out the experiment with somewhat different proportions of the components, namely with the mixture: 7.8 g of β-naphthaldehyde (0.05 mole), 5.72 g of malonic acid (0.055 mole), 5.78 g of ammonium acetate (0.075 mole), and 20 ml of glacial acetic acid, and working up as in experiment c, 5.59 g of β-(β-naphthyl)-β-alanine, i.e. 58.8% of theoretical, and 3.06 g of β-(β-naphthyl)-acrylic acid, i.e. about 31% of theoretical, were obtained.

The methyl ester of β-(β-naphthyl)-β-alanine. β-(β-Naphthyl)-β-alanine (8.6 g), methanol (80 ml), and conc. H_2SO_4 (12 ml) were heated for 4 hours on a water bath; methyl alcohol (50 ml) was then driven off. On cooling, the residue was neutralized with a soda solution. The oil that separated rapidly crystallized. The crystals were filtered off, washed with water, and then recrystallized from diluted methyl alcohol. Yield 7.39 g, i.e. about 80% of theoretical. Melting point of the ester after recrystallization from ligroin, 94-95°.

Found %: C 72.96; 73.19; H 6.66; 6.79; N 6.20; 6.16.
$C_{14}H_{15}O_2N$. Calculated %: C 73.74; H 6.60 N 6.11.

The methyl ester is formed as large glistening prisms from ligroin. It is readily soluble in alcohol, ether, benzene, acetone, and in dilute mineral acids; in ligroin it is difficulty soluble in the cold, but fairly soluble on warming. It is readily hydrolyzed on boiling with alkali to a salt of the β-amino acid. On standing for many days in ammoniacal alcoholic solution, it is converted into the amide of β-(β-naphthyl)-β-alanine. The alcoholic solution was filtered from small amounts of contamination and gave, after driving off the alcohol, an approximately 65% yield of not altogether pure amide, m.p. 142-143°. Recrystallization from water raised the m.p. to 143.5-144.5°. Analysis for nitrogen showed that the compound obtained was not quite homogeneous.

Found %: N 12.6; 12.41
$C_{13}H_{14}ON_2$. Calculated %: N 13.08

N-Benzoyl-β-(β-naphthyl)-β-alanine. β-(β-Naphthyl)-β-alanine (6.45 g) was dissolved in 150 ml of a 4% solution of caustic soda, and benzoyl chloride (4.2 ml) was added gradually from a dropping funnel to the ice-cooled solution. The solution obtained was left overnight, then filtered from the small amount of suspended matter, extracted twice with ether, and acidified with hydrochloric acid. The precipitate that immediately formed was filtered off some hours later and was washed with water. In order to remove benzoic acid, the precipitate was boiled with water, filtered off, washed with hot water on the filter, and then recrystallized from aqueous alcohol. Yield 8.65 g, i.e. 90.3% of theoretical.

N-Benzoyl-β-(β-naphthyl)-β-alanine crystallizes in fine glistening prisms (from aqueous alcohol); m.p. 209-210°. It is insoluble in water, ether, benzene, and mineral acids. It readily dissolves in alkalis, acetone, methanol, and ethanol.

Found %: C 75.46; 75.35; H 5.34; 5.21; N 4.53; 4.33
$C_{20}H_{17}O_3N$. Calculated %: C 75.22; H 5.37 N 4.39

N-Acetyl-β-(β-naphthyl)-β-alanine. Acetic anhydride (15 ml) was added from a dropping funnel to an ice-cooled mechanically stirred solution of 10.75 g of β-(β-naphthyl)-β-alanine in 160 ml of a 10% solution of caustic soda. The reaction mixture was left overnight and was then acidified with hydrochloric acid. The voluminous precipitate that immediately formed was filtered off some hours later, washed with water, and dried to constant weight. Yield 12.76 g; m.p. 164-174°. After recrystallizing once from alcohol, the acetyl derivative appeared to be quite pure and melted sharply at 177.5-178.5°. It crystallizes from alcohol in glistening colorless prisms. It dissolves readily in alkalis, acetone, methanol, and ethanol; with difficulty in water, ether, and benzene. Yield of recrystallized product 10.16 g, i.e. 77% of theoretical.

Found %: N 5.46; 5.45
$C_{15}H_{15}O_3N$. Calculated %: N 5.45

Anilide and amide of N-acetyl-β-(β-naphthyl)-β-alanine. A mixture of 7.72 g of N-acetyl-β-(β-naphthyl)-β-alanine, which was finely ground and dried in a vacuum desiccator, and 5 ml of thionyl chloride was heated on the water-bath at 40-50° until gas evolution ceased. The excess of thionyl chloride was driven off in a vacuum at 40-50°. The residue in the flask was a red, very viscous oil, difficultly soluble in absolute ether.

Anilide: A small quantity of the prepared acid chloride was treated with a small excess of aniline in ethereal solution at room temperature. The powder-like precipitate formed was filtered off and extracted successively with dilute HCl, caustic soda, and finally water. After one recrystallization from alcohol, 0.14 g of a substance of m.p. 236-237° was obtained. After a further recrystallization the product melted at 237-238°. The anilide crystallizes from alcohol in colorless prisms. It is insoluble in water, acids, alkalis, ether, and benzene; rather difficultly soluble in cold methanol, ethanol, and acetone, but dissolves more readily on heating.

Found %: N 8.75; 8.60

$C_{21}H_{20}O_2N_2$. Calculated %: N 8.43

Amide. Strong aqueous ammonia (150 ml) was added to the main mass of the acid chloride. The mixture was shaken vigorously for 30 min. and then left to stand for several hours; the precipitate that had formed was then filtered off and well washed with alkali and water. The dried precipitate was ground and recrystallized from dilute alcohol. 5.66 g of amide, m.p. 255.5-227.5°, was obtained. By repeated recrystallization from a mixture of water and alcohol (5:1), constant m.p., 230-231°, was attained. The amide of N-acetyl-β-(β-naphthyl)-β-alanine crystallizes from aqueous alcohol in glistening long plates. It does not dissolve in ether or benzene; it is of rather poor solubility in methanol, ethanol, and acetone in the cold, but dissolves readily on warming; it is almost insoluble in cold water, but dissolves in hot water.

From the mother liquor, after evaporation and acidification, 0.76 g of the original β-(β-naphthyl)-β-alanine was isolated. Thus, the yield of amide calculated on the amount of β-(β-naphthyl)-β-alanine that reacted (7.72-0.76) is 5.56 g, i.e. about 80-81% of theoretical (not taking into account the amount of acid chloride taken for preparing the anilide.)

N-Methyl-β-(β-naphthyl)-β-alanine

a) β-Naphthaldehyde (1.56 g), malonic acid (1.30 g), methylamine hydrochloride (1.01 g), anhydrous potassium acetate (1.50 g), and glacial acetic acid (5 ml) were heated on a boiling water bath for 8-9 hours. The originally homogeneous mixture evolved gas with formation of a crystalline precipitate. The thick crystalline mass obtained after cooling was extracted with dil. HCl (see synthesis of β-(β-naphthyl)-β-alanine). The hydrochloric acid filtrate was first concentrated on the water-bath and then extracted 4-5 times with ether and neutralized with a concentrated solution of sodium acetate. After a few hours, the precipitate that separated was filtered off, washed with water, and dried at 70-80°. 1.20 g of a substance of m.p. 187-188° (with decomposition) was obtained. After purifying for analysis by repeated crystallization, the substance melted at 195-195.5° (with decomposition).

N-Methyl-β-(β-naphthyl)-β-alanine crystallizes in prisms; it is easily soluble in mineral acids and in alkalis, and also, on boiling, in water and in acetone.

Found %: N 5.82; 5.91

$C_{14}H_{15}O_2N$. Calculated %: N 6.11

The crystalline residue that remains on the filter after extracting the reaction mixture with hydrochloric acid was found to be pure β-(β-naphthyl)-acrylic acid, m.p. 207-208°. Yield 0.78 g (about 39% of theoretical).

b. Preparation from N-(β-naphthal)-methylamine. Dry N-(β-naphthal)-methyl-β-amine (1.69 g), malonic acid (1.04 g), and ethyl alcohol (5 ml) were boiled on the water-bath for 10 hours. Full dissolution occurred in the first 10 min., and a large amount of gas was evolved. After 30 min., a precipitate started to appear. After cooling, the reaction mass was treated in the way indicated above. Yield of crude N-methyl-β-(β-naphthyl)-β-alanine (m.p. 189-190°) 0.68 g, i.e. 29.5% of theoretical. Yield of crude β-(β-naphthyl)-acrylic acid, 1.14 g, i.e. about 57.5% of theoretical.

SUMMARY

1. The method of preparing β-naphthaldehyde proposed by Sultanov, Rodionov, and Shemyakin, based on the oxidation of β-methylnaphthalene with selenium dioxide, has been improved by the use of naphthalene as solvent. The yield of aldehyde rose from 34 to 66-67% of theoretical.

2. N-(β-Naphthal)-methylamine and methyl β-(β-naphthyl)-acrylate are described for the first time.

3. The following have been synthesized: β-(β-naphthyl)-β-aminopropionic acid, its methyl ester, its amide, and its benzoyl and acetyl derivatives; the amide and anilide of N-acetyl-β-(β-naphthyl)-β-aminopropionic acid; and N-methyl-β-(β-naphthyl)-β-aminopropionic acid.

β-(β-Naphthyl)-β-aminopropionic acid has been prepared by the basic reaction of Rodionov and also by three variants of this method.

4. N-Methyl-β-(β-naphthyl)-β-aminopropionic acid has been prepared by two methods; one of them is new.

D.I.Mendeleev Chemico-Technological Institute. Received August 31, 1951

LITERATURE CITED

[1] I.S. Belonosov. Degree thesis, Moscow, 1939.

[2] N.A. Kravchenko. Degree thesis, Moscow, 1950.

[3] J. Batterschall. Ann., 168, 114 (1875).

[4] A.E.Chichibabin. Ber., 44, 447 (1911).

[5] Peter Sah. Rec. trav. chim., 59, 1021 (1940).

[6] F. Meyer and A. Stieglitz. Ber., 55, 1857 (1922).

[7] J. Fulton and R.Robinson. J.Chem.Soc., 1939, 200; J.Williams. Org. Synth., 23, 63 (1943).

[8] E.Hershberg and J.Cason. Org. Synth., 21, 84 (1941).

[9] V.M.Rodionov, and M.A.Berkengeym. J.Gen.Chem., 14, 330 (1944); A.S. Sultanov, V.M.Rodionov, and M.M.Shemyakin. J.Gen.Chem., 16, 2072 (1948). See also the monograph by N.I.Melnikov "Selenious Anhydride as an Oxidizing Agent in Organic Chemistry" in the Collection of "Reactions of Organic Compounds", vol. 1. Moscow, State Chemistry Press, 1951, pp. 99-178.

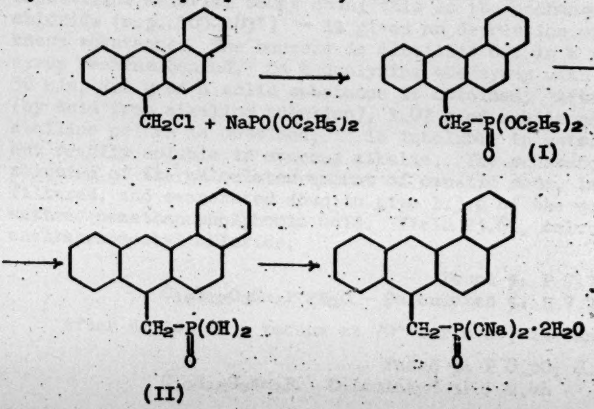
[10] T.Johnson and J.Evans. J.Am.Chem.Soc., 52, 4993 (1936); T.Johnson, Rec. trav. chim., 48, 872 (1929).

SYNTHESIS OF 7-BENZ[a]ANTHRACENEMETHANEPHOSPHONIC AND 12-METHYL-7-BENZ[a]ANTHRACENEMETHANEPHOSPHONIC ACIDS1)

B. A. Arbuzov and N. P. Grechkin

The carcinogenic hydrocarbons are oil-soluble, water-insoluble substances. Injection of carcinogenic substances in oil into the organism causes the undesirable formation of oleomas, i.e. tumors produced by the oil itself. For this reason attempts have been made to obtain substances having the skeleton of the carcinogenic hydrocarbons, but soluble in water. Thus there are the soluble complexes of carcinogenic hydrocarbons with desoxycholic acid [1], which were found to be of little use, owing to the fact that desoxycholic acid is a powerful hemolytic poison. Phenols derived from the carcinogenic hydrocarbons were found to be inactive [2]. There are also the compounds of the carcinogenic hydrocarbons with maleic anhydride, the salts of which are soluble in water [3], etc.

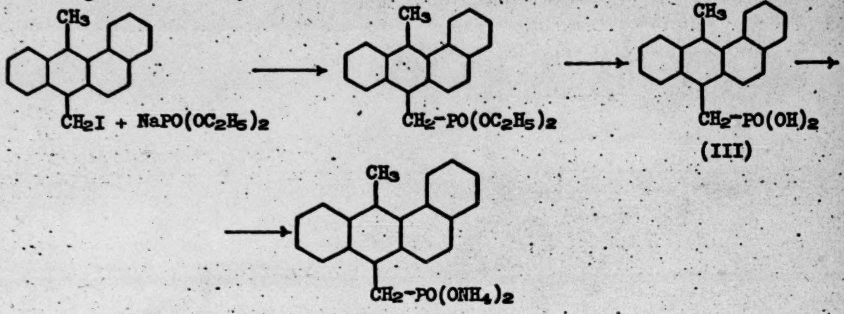
It seemed to us that, considering the important part played by organic derivatives of phosphorus in the organism, it would be interesting to prepare derivatives of actively carcinogenic substances containing the phosphonic group. Such acids or their salts might be soluble in water. With this in view we have examined the action of sodium diethyl phosphite on 7-benz[a]anthracenemethyl chloride. The resulting ester of the corresponding phosphonic acid (I) gave on hydrolysis the free phosphonic acid, whose sodium salt is soluble in water.



---

1) Paper read at a session of the Division of Chemical Sciences and of the Division of Physico-mathematical and Chemical Sciences of the Academy of Sciences of the Ukrainian S. S. R. in Kiev, June 1950.

From 12-methyl-7-benz[a]anthracenemethyl iodide, the corresponding phosphonic acid (III) was prepared through the ester in an analogous manner; its ammonium salt is of good solubility in water:



The substance III is a derivative of one of the most powerfully carcinogenic substances, 7,12-dimethylbenz[a]anthracene.

EXPERIMENTAL

Action of sodium diethyl phosphite on 7-benz[a]anthracenemethyl chloride

7-Benz[a]anthracenemethyl chloride (4 g) [4] is added to a benzene solution of the calculated amount of sodium diethyl phosphite at room temperature. The crystals of the former rapidly disappear, and the solution takes up a bright yellow color. The solution is boiled for an hour; the color of the solution becomes less intense, and a white precipitate forms on the walls of the flask. The solution is poured off, and the precipitate is washed with benzene by decantation. After the solution has stood for a short time, a small amount of crystalline material comes down; this is the unchanged benzanthracenemethyl chloride (m.p. 185-187°) – it gives no depression of m.p. in admixture with known substance. The benzene is distilled off in a vacuum, and a yellowish thick syrup remains behind. On hydrolyzing the syrup with conc. HCl under reflux for 30 min, 2.1 g of a solid substance is obtained. After reprecipitating twice (by acid from alkaline solution), 1.07 g of substance in the form of microcrystalline prisms is obtained; it is insoluble in water and in hydrochloric acid, but readily soluble in aqueous alkalis. The substance, dissolved in an aqueous solution of the calculated amount of caustic soda, is boiled with charcoal, filtered, and evaporated down to give 1.3 g of the sodium salt of 7-benz[a]-anthracenemethanephosphonic acid. Yield 23.6%, calculated on the original benzanthracenemethyl chloride.

Found %: P 7.72; 7.69
$C_{19}H_{12}O_3Na_2P\cdot 2H_2O$. Calculated %: P 7.73

After drying in a vacuum at 70° for 6 hr, the analysis was repeated:

Found %: P 8.50; 8.41
$C_{19}H_{12}O_3Na_2P$. Calculated %: P 8.46

Action of sodium diethyl phosphite on 12-methyl-7-benz[a]anthracenemethyl iodide

12-Methyl-7-benz[a]anthracenemethyl iodide (4.9 g) [5] is added in the cold to a solution of 2.1 g of sodium diethyl phosphite in 50 ml of dry benzene. Reaction, with separation of sodium iodide, proceeds even in the cold. After boiling the solution for 15 min, the sodium iodide is filtered off (1.85 g = 95% of theoretical). The filtrate is a yellowish transparent liquid. The benzene is distilled off in a vacuum leaving a thick syrup. The latter is hydrolyzed with boiling conc. HCl under reflux for 24 hr, and a brownish solid (4 g) is obtained. After dissolving this in aqueous alkali and precipitating with hydrochloric acid, 2.1 g of a crystalline substance in the form of fine yellowish needles is obtained. This substance is dissolved by heating with excess of 25% ammonia. After evaporating the solution, 1.5 g of yellowish leaf-like crystals is obtained. Yield 30.6%, calculated on the original methylbenzanthracenemethyl iodide.

Found %: P 8.43; 8.56
$C_{20}H_{23}ON_2P$. Calculated %: P 8.38

SUMMARY

The following phosphonic acids and their ethyl esters have been synthesized: 7-benz[a]anthracenemethanephosphonic acid and 12-methyl-7-benz[a]anthracenemethanephosphonic acid. These are derivatives of actively carcinogenic compounds.

A. E. Arbuzov Chemical Institute
Kazan Affiliate of the
U.S.S.R. Academy of Sciences

Received April 17, 1951

LITERATURE

[1] J. W. Cook and co-workers. Proc. Roy. Soc. 111, 455; 111, 486 (1932); 117, 318 (1935); Parsons, J. Path. Bact. 431 (1936); L. Fieser and Newman, J. Am. Chem. Soc. 57, 961 (1935); Winterstein and Vetter Z. physiol. Chem. 230, 169 (1934).

[2] J. W. Cook, J. Chem Soc. 3273 (1931); I. Berenblum and co-workers, Cancer Res. 3, 145; 3, 151 (1943).

[3] H. Burrows and J.W.Cook, Am. J. Cancer 27, 267 (1936).

[4] Badger and J. Cook, J.Chem.Soc., 802 (1939).

[5] R. B. Sandin and L.F.Fieser, J.Am. Chem. Soc., 62, 3102 (1940).

BLANK
PAGE

INVESTIGATION OF ANTHRACENE DERIVATIVES

COMMUNICATION 10. THE RELATIVE ACTIVITIES OF THE MESO CARBON ATOM OF ANTHRACENE AND 9,10-DICHLOROANTHRACENE IN REACTIONS WITH OXIDIZING AGENTS

B. P. Fedorov and N. V. Ptitsina

One of us [1,2] has already shown that in the preparation of anthraquinone by oxidizing anthracene in aqueous suspension with chlorine the reaction finally slows down considerably when the main component of the mixture, apart from anthraquinone, becomes 9,10-dichloroanthracene, which is a by-product in the reaction. As the concentration of chlorine in the solution was maintained constant, we considered that the slowing down was to be explained by the greater reluctance of 9,10-dichloroanthracene to undergo oxidation, as compared with anthracene itself. In this connection, we have now determined the reaction rates for the oxidation of anthracene and of 9,10-dichloroanthracene by chlorine water and have shown that reaction with anthracene is many times more rapid than with 9,10-dichloroanthracene. At the same time we have shown that also with other oxidizing agents, e.g. $K_2Cr_2O_7 + H_2SO_4$ and $KMnO_4 + KOHaq$, reaction with anthracene is considerably more rapid than with 9,10-dichloroanthracene. The course of the reaction was followed by determining the concentration of oxidizing agent in solution at definite intervals of time. The relative rates of oxidation of anthracene and of 9,10-dichloroanthracene and the relative activities of the meso-carbon atoms of these compounds in these reactions were estimated according to the consumption of oxidizing agent.

EXPERIMENTAL

Starting materials. Anthracene, chemically pure, m.p. 216°, was prepared by recrystallizing 93-94% anthracene twice from benzene, distilling, and then again crystallizing from toluene. 9,10-Dichloroanthracene was prepared by the method already described by one of us [3]. After three crystallizations from benzene, the first in conjunction with activated wood charcoal, 9,10-dichloroanthracene was obtained in the form of pale-yellow needles, m.p. 212.4°. Further crystallization did not affect the melting point.

In view of the fact that the reactions under investigation are carried out under heterogeneous conditions, it was necessary, in order to obtain comparative results, to pay particular attention to regularity of particle size, standard pasting procedure, and standard conditions for stirring during reaction. Only by careful observation of standard conditions in these operations was it possible to obtain results agreeing within 2-3% in duplicate experiments.

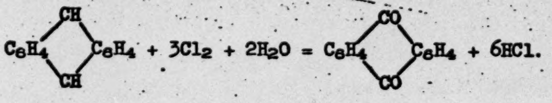
Anthracene and 9,10-dichloroanthracene were carefully ground, first in the dry state, and then as an aqueous paste, which was rubbed through silk gauze having 64 mesh per cm. The pastes obtained were pressed off on a filter, dried, and again ground. For the preparation of chlorine water, chlorine from a cylinder was used. Chemically pure dichromate and permanganate were used.

I. Oxidation with Chlorine Water

Experimental Procedure. The determination of the rate of the reaction of anthracene (9,10-dichloroanthracene) with chlorine water was carried out in a flask of about 400 ml capacity with a ground-in stopper; the flask was fixed by the aid of screw clamps in a vertical position in a jacket with a rubber seal. The jacket was attached to a shaker, which gave 70-75 shakes per min. Depending on the conditions of the experiment, either water or a cooling mixture was passed through the jacket; the temperature of the cooling agent was measured as the latter went in and came out of the jacket. The flask was checked for leaks by means of blank experiments in which chlorine water only was shaken for some hours and its concentration determined. The chlorine water was prepared by saturating freshly distilled water with chlorine from a cylinder, and it was kept in a vessel of dark-colored glass with a ground-in stopper. The required concentration of chlorine was obtained by subsequently diluting the solution with distilled water, and before each experiment the concentration was checked by iodometric titration. The required amount of chlorine water was taken with the aid of a special, previously calibrated pipet, similar in construction to Yakovkin's pipet [4], with a three-way tap and bulb, designed to remove the top layer of the chlorine water that is drawn up.

The weighed amount of anthracene (9,10-dichloroanthracene), ground up in the manner already described, is pasted up with 0.5 ml of water in a thin glass test-tube and introduced into the reaction flask, into which, after allowing about half an hour for the temperature of the experiment to be reached, a definite volume of chlorine water is introduced by the aid of the pipet. The reaction is considered to start at the moment when the anthracene (9,10-dichloroanthracene) is introduced: on shaking, the test tube is broken, and the substance under investigation is uniformly distributed in the chlorine water.

After a definite interval of time the shaker is stopped and the course of the reaction is interrupted by adding an excess of 10% KI; the iodine liberated is titrated with thiosulfate. In some of the experiments the acidity of the solution was determined alkalimetrically (after the iodometric titration) in presence of phenolphthalein. For each period of time, at least two experiments were carried out for each temperature. Most of the experiments were carried out with an excess of anthracene over that calculated from the equation for oxidation to anthraquinone:



$$C_6H_4\overset{CH}{\underset{CH}{<\;>}}C_6H_4 + 3Cl_2 + 2H_2O = C_6H_4\overset{CO}{\underset{CO}{<\;>}}C_6H_4 + 6HCl. \qquad (1)$$

According to this equation, 33.69 ml of 0.1 N chlorine is required for 0.1 g of anthracene. The amount of chlorine consumed in the oxidation was determined from the difference between the amount of chlorine taken for the experiment and the amount remaining after the reaction, working in ml of 0.1 N solution and recalculating as % of the amount of chlorine required for complete oxidation. The results of experiments in which the effect of the chlorine concentration and the temperature on the rate of oxidation of anthracene is studied are given in Tables 1, 2, 3, 4, and 5 and in Fig. 1. The results of experiments on the oxidation of 9,10-dichloroanthracene by chlorine water are given in Table 6 and Fig. 1.

The following are the signs used in the tables and in the text: t is the time from the start of the experiment (min); A_0 is the volume of 0.1 N chlorine water at the start of the experiment (ml); $A_0 - x$ is the volume of 0.1 N chlorine water remaining after the oxidation (ml); x is the volume of 0.1 N chlorine water consumed in the oxidation (ml); k_1 is the value of the first-order constant calculated from the equation:

$$k_1 = \frac{2.303}{t} \log \frac{A_0}{A_0 - x} \tag{2}$$

and k_2 is the value of the first-order constant calculated from the equation:

$$k_2 = \frac{1}{t} \left[2.303\, A_0 \log \frac{A_0}{A_0 - x} - x \right]. \tag{3}$$

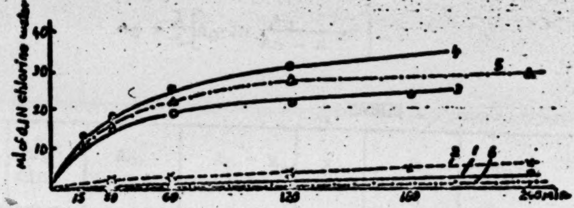


Fig. 1. Oxidation of anthracene (curves 1-5) and of 9,10-dichloroanthracene (curve 6) by chlorine water: 1) 50.07 ml 0.01 N chlorine water, t 2-3°; 2) 50.07 ml 0.05 N chlorine water, t 2-3°; 3) 50.07 ml 0.05 N chlorine water, t 15-16°; 4) 99.31 ml 0.05 N chlorine water, t 15-16°; 5) 99.31 ml 0.05 N chlorine water, t 15-16° in presence of hydrochloric acid; 6) 50.07 ml 0.05 N chlorine water, t 20-21°

In spite of the complex nature of the processes occurring in the heterogenous system investigated, we have attempted to give our measurements a kinetic treatment, and we have obtained comparatively satisfactory results by treating the reaction as being formally of the first order with respect to active chlorine. For the purpose of the kinetic investigation of the oxidation of anthracene, we took into account the courses of the chemical reactions, but not the processes occurring at the bounding surfaces and also not the diffusion processes, although, as the experiments show, the latter play an essential role.

From an examination of the experimental results in the tables and in Fig. 1, the following preliminary conclusions can be made:

1) The reaction rate increases approximately proportional to the analytically determined concentration of active chlorine (Tables 1 and 2).

2) The reaction rate is reduced by the hydrochloric acid that is formed or is introduced prior to the reaction (Fig. 1, curves 4 and 5; Tables 1-5).

3) The reaction rate for the oxidation of anthracene is considerably greater than that for the oxidation of 9,10-dichloroanthracene (Fig. 1, curves 3 and 6; Tables 3 and 6).

In order to derive a kinetic equation on the basis of this information we must take into consideration that the rate of change of the concentration of oxidizing agent at any given moment is proportional to the analytically determined concentration of active chlorine and inversely proportional to the concentration of hydrochloric acid:

$$-\frac{d[Cl_2]}{dt} = k_2^1 \frac{[Cl_2]}{[HCl]} .$$

Introducing our symbols and converting to a form that is suitable for integration:

$$-\frac{d[A_0 - x]}{dt} = k_2^1 \frac{[A_0 - x]}{[x]} \text{ and } \frac{xd[A_0 - x]}{A_0 - x} = -k_2dt.$$

After integration this equation assumes the form:

$$k_2 = \frac{1}{t}\left[A_0 \ln \frac{A_0}{A_0 - x} - x\right] . \qquad (4)$$

TABLE 1

Expt. No.	t, min.	A_0, ml	$A_0 - x$, ml	x, ml	k_1	k_2	Percent of amount theoretically necessary for oxidation
1	15	5.95	5.65	0.30	0.0034	0.00054	0.89
2	30	5.96	5.53	0.43	0.0025	0.00054	1.27
3	60	5.98	5.36	0.62	0.0018	0.00057	1.84
4	120	6.00	5.10	0.90	0.0010	0.00062	2.67
					Mean	0.00056	

Amount of anthracene taken, 0.1 g; 50.07 ml of chlorine water was taken for each experiment; temperature of experiment 2-3°.

TABLE 2

Expt. No.	t, min.	A_0, ml	$A_0 - x$, ml	x, ml	k_1	k_2	Percent of amount theoretically necessary for oxidation
1	30	26.19	24.41	1.78	0.0023	0.0021	5.27
2	60	27.09	24.55	2.54	0.0016	0.0021	7.53
3	120	25.78	22.54	3.24	0.0011	0.0019	9.40
4	180	25.88	21.72	4.16	0.0009	0.0021	12.28
					Mean	0.0021	

Amount of anthracene taken, 0.1 g; 50.07 ml of chlorine water was taken for each experiment; temperature of experiment 2-3°.

From this equation we calculated the rate constants for the reaction. These are given in Tables 1, 2, 3, 4, and 5. It must be pointed out that the calculated reaction rate constants are conventional only, but are of significance for comparative purposes.

If, however, the rate constant is calculated from the equation

$-\frac{d[Cl_2]}{dt} = k_1[Cl_2]$, then a constant is obtained that falls rapidly, as will be seen from the tables. For convenience of discussion, the results obtained are brought together in Table 7.

As will be seen from Series 1 and 2, the rate constant is approximately proportional to the concentration of active chlorine. On the other hand, increase in the amount of chlorine at a given temperature and for a given concentration of active chlorine may even cause a fall in the constant for the series (Series 3 and 4), which is probably to be explained by the increase in the volume of the liquid phase. A 1° rise in temperature results in a ten-fold increase in the rate constant. The hydrochloric acid formed reduces the reaction rate (Tables 1-4), and the prior introduction of hydrochloric acid to the extent of about 0.02 mole causes a fall in the constant by about 10% (Series 4 and 5).

TABLE 3

Expt. No.	t, min.	A_0, ml	$A_0 - x$, ml	x, ml	k_1	k_2	Percent of amount theoretically necessary for oxidation
1	15	25.93	14.52	11.41	0.03866	0.2420	33.8
2	30	25.93	10.82	15.11	0.02915	0.2520	44.8
3	60	25.89	6.79	19.10	0.02231	0.2594	55.4
4	120	25.95	3.86	22.09	0.01588	0.2280	65.5
					Mean	0.2452	

Amount of anthracene taken, 0.1 g; 50.07 ml of chlorine water was taken for each experiment; temperature of experiment 15-16°.

TABLE 4

Expt. No.	t, min.	A_0, ml	$A_0 - x$, ml	x, ml	k_1	k_2	Percent of amount theoretically necessary for oxidation
1	15	48.82	35.10	13.72	0.02200	0.1592	40.7
2	30	48.36	30.40	17.96	0.01548	0.1494	53.3
3	60	51.44	26.66	24.78	0.01095	0.1505	73.5
4	120	49.24	18.98	30.26	0.00790	0.1392	89.8
5	240	48.96	17.55	31.41	0.00430	0.0784[1]	93.2
					Mean	0.1495	

[1] Rejected when calculating mean.

Amount of anthracene taken, 0.1 g; 99.31 ml of chlorine water was taken for each experiment; temperature of experiment 15-16°.

When the percentage conversion of the anthracene reaches about 90, a sharp fall in the value of the constant is observed; this occurs in Experiment 5, Table 4 and in Experiment 4, Table 5. This fall in the constant is to be explained by the accumulation in the reaction products of 9,10-dichloroanthracene; the rate of the oxidation of 9,10-dichloroanthracene is many times less than that of anthracene under the same conditions of temperature and chlorine concentration (Fig. 1, curves 3 and 6; Tables 3 and 6).

TABLE 5

Expt. No.	t, min.	A_0, ml	$A_0 - x$, ml	x, ml	k_1	k_2	Percent of amount theoretically necessary for oxidation
1	30	45.65	29.04	16.61	–	0.1340	49.30
2	60	46.18	23.42	22.76	–	0.1430	67.54
3	120	46.48	18.05	28.43	–	0.1300	84.36
4	240	46.16	29.94	29.94	–	0.0740[1]	88.84
					Mean	0.1356	

[1] Rejected when calculating mean.

Amount of anthracene taken, 0.1 g; 99.31 ml of chlorine water was taken for each experiment. The experiments were carried out in presence of hydrochloric acid, concentration 0.02232 mole per liter; the temperature of the experiment was 15-16°.

TABLE 6

Expt. No.	t, min.	A_0, ml	$A_0 - x$, ml	x, ml	k_1	k_2	Percent of amount theoretically necessary for oxidation
1	60	30.38	30.26	0.12	–	–	1.48
2	120	30.53	30.30	0.22	–	–	2.71
3	180	30.82	30.34	0.48	–	–	5.92
4	240	29.92	29.36	0.56	–	–	7.08

Amount of 9,10-dichloroanthracene taken, 0.1 g: 50.07 ml of chlorine water was taken for each experiment; temperature of experiment, 20-21°.

TABLE 7

Expt. Series No.	Temp. (°C)	Moles chlorine per mole of anthracene	Concentration of chlorine water	k_2	Ratio of constants	
1	2-3	1.07	0.012	0.00056	$k_2^2:k_2^1$	=3.75[1]
2	2-3	4.67	0.0524	0.0021	$k_2^3:k_2^1$	=1.17
3	15-16	4.62	0.0518	0.2452	$k_2^3:k_2^4$	=1.64
4	15-16	8.91	0.0504	0.1495	$k_2^4:k_2^5$	=1.1
5	15-16	8.91	0.0504	0.1356		

[1] The superscript numbers indicate the number of the series.

The Products Obtained by the Action of Chlorine on Anthracene in Aqueous Suspension

When halogens react with anthracene and other organic compounds in aqueous suspension, or in suspension in aqueous solutions of alcohol, acetone, or acetic acid, mainly oxidative processes occur.

Meyer [5] and Zahn [6], by the action of chlorine or bromine on anthracene suspended in aqueous solutions of alcohol or acetic acid at 25°, obtained oxanthranol, which was converted into anthraquinone by the prolonged action of chlorine; at a high temperature, the main reaction was the oxidation of anthracene to anthraquinone. They observed also the formation of 9,10-dichloroanthracene as a by-product. Plazek [7], by the action of chlorine on anthracene in methanol or ethanol, obtained anthraquinone in very good yield and in a high state of purity. Charrier and Grippa [8], by the action of hypochlorous acid on anthracene in aqueous suspension, obtained a product that they took to be a mixture of 9-hydroxy-10-chloroanthracene and 9-hydroxy-10-chlorodihydroanthracene. The mixture of these products was converted by boiling with alcohol into bis(9-hydroxy-10-anthryl) ether. Price and Weaver [9], by the action of bromine on anthracene in dry acetone, obtained a good yield of 9,10-dibromoanthracene (m.p. 221°). When the acetone employed was not carefully dried, the products were always 9-bromoanthrone (m.p. 142-144°) and anthraquinone (m.p. 280-282°), and when the water content of the acetone was high, anthraquinone was the sole product.

We have investigated the products obtained by the action of 1200 ml of a 0.05 N aqueous solution of chlorine on 2.5 g of anthracene at 15-16° for 60 hours and have isolated the following products:

1. The reaction product was treated several times with a hot 4-5% solution of caustic soda until the filtrate ceased to have a red color. When the color became brownish yellow, the caustic soda solution was diluted to 0.5%, and extraction was continued until a colorless filtrate was obtained. On acidifying the red filtrate with dil.HCl or H_2SO_4, a brownish-yellow substance was precipitated, and from this, by crystallization from glacial acetic acid, two substances were isolated.

a) The first (about 1%) crystallized out after cooling the acetic acid solution and was obtained, after recrystallization, in the form of yellow needles, m.p. higher than 300°. The substance does not contain chlorine and yields anthraquinone, m.p. 285°, on oxidation with chromic acid in acetic acid. It gives a bluish-red solution in conc.H_2SO_4. Its structure was not established.

Found %: C 87.1; H 4.1

b) The second substance (about 7%), which was isolated by diluting the filtrate, was obtained, after crystallizing twice from alcohol, in the form of light-yellow crystals, melting over the range 161-170°; it was identified as a mixture of 9,10-dihydroxyanthracene and oxanthranol. The substance does not contain chlorine, dissolves in a 3-4% solution of caustic soda to give a red solution, and rapidly oxidizes to anthraquinone. It gives a wine-red solution in sulfuric acid. A mixed melting point with synthetic 9,10-dihydroxyanthracene shows no depression.

By acidification of the brownish-yellow filtrate, a substance was isolated, which was identified with anthranol (about 3%). After crystallization from alcohol, it was obtained in the form of brownish-yellow needles, m.p. 161-167°. The substance does not contain chlorine, gives a brownish-yellow solution in alkali, and is oxidized by chromic acid to anthraquinone. It gives a greenish-yellow solution in conc. H_2SO_4, which becomes bluish-red on the addition of nitric acid. It shows a blue fluorescence in alcoholic solution. Positive results are obtained in the characteristic reaction for anthranol [10]: by the action of fuming nitric acid a substance is formed that, after precipitation with water, may be dissolved in alcohol to give an orange solution; this solution becomes violet on addition of alkali.

2. The residue after the treatment with aqueous alkali was treated repeatedly with a solution containing, per 100 ml, 8 g of sodium hydrosulfite and 8 g of caustic soda at a temperature of 60-80°. After oxidation of the red filtrate by means of the oxygen of the air, anthraquinone (61-62%), m.p. 285-286°, was precipitated.

3. The residue after the separation of alkali-soluble compounds and of anthraquinone comprised about 25% of the anthracene taken and consisted of anthracene and 9,10-dichloroanthracene, the amounts of which were determined in the following way: the material was recrystallized from a very small amount of glacial acetic acid, and the product (0.3574 g, m.p. 160-170°) was dissolved in 10 ml of glacial acetic acid and heated with a solution of 5.4 g of CrO_3 in 8 ml of 50% acetic acid for 20 min; the solution was then poured into 100 ml of ice-water, and the precipitated anthraquinone was filtered off, washed, and dried. Weight of anthraquinone, m.p. 286°, 0.3630 g. Hence we find: anthracene 53.2%, and 9,10-dichloroanthracene 46.8%

Found %: Cl 13.41 (Carius)
Calculated %: Cl 13.7 (according to the composition found).

After several crystallizations of the remaining mixture, anthracene, m.p. 214-215°, and 9,10-dichloroanthracene, m.p. 208-209°, were isolated. Consequently, by the action of chlorine water on anthracene at 15-16° for 50-60 hours, a mixture of products were obtained, among which the following were found:

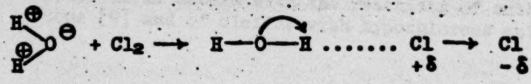
Anthraquinone	61-62%
Anthrahydroquinone and oxanthranol	7%
Anthranol	3%
9,10-Dichloroanthracene	~ 12%
Anthracene (unreacted)	13%
Substance, m.p. > 300°	~ 1%.

Some observations on the mechanism of the reaction. As is well known, anthracene is peculiar in its chemical behavior in that the initial reactions generally consist in addition reactions of various species to the meso carbons of anthracene, and anthracene stands more closely in this respect to the olefins than to the aromatic hydrocarbons. Thus, when halogenated, nitrated, hydrogenated, or metalized, and in diene syntheses and in the formation of photo-oxides, anthracene forms, in the first stage, stable addition products, whereas no such addition products have been isolated in the analogous reactions of benzene and naphthalene. We consider that in the oxidation of anthracene the first step in the reaction is the formation of addition products of anthracene, although some of these (e.g. 9,10-dihydroxydihydroanthracene) have not been isolated in the free condition.

We consider that when anthracene reacts with chlorine water two simultaneous oxidation processes occur: in one of these chlorine takes part, and in the other – hypochlorous acid. This idea is in agreement with Shilov's views [11] on the process of chlorine bleaching, which he has developed from the kinetics of the addition of hypochlorous acid at a double bond [12]. According to

Shilov, the reaction of chlorine water with a reducing agent is to be treated as a complex process, comprising oxidation, addition, and chlorination reactions. Let us consider the two processes.

1. One of us [2] has previously suggested that the oxidizing agent in chlorine water is the molecule of chlorine at the moment of its reaction with water. We have assumed a mechanism for the oxidation of anthracene by chlorine water in which chlorine molecules that have been polarized by the electric field of water molecules take part:



$$\overset{\oplus}{H}\overset{\ominus}{O}\overset{\oplus}{H} + Cl_2 \rightarrow \overset{\curvearrowright}{H-O-H} \,.......\, \underset{+\delta}{Cl} \rightarrow \underset{-\delta}{Cl} \qquad (6)$$

Thus we assume that in the equilibrium existing in chlorine water we have, as well as chlorine molecules, water, hypochlorous acid, hydrogen ions, and chlorine, also chlorine molecules that are polarized in the electric field of water molecules, in accordance with the following equilibrium equations:

$$Cl_2 + H_2O \rightleftharpoons \overset{\curvearrowright}{H-O-H} \,.......\, \underset{+\delta}{Cl} \rightarrow \underset{-\delta}{Cl} \rightleftharpoons HOCl + H^+ + Cl' \qquad (7)$$

The mechanism of the oxidation of anthracene by chlorine water with the participation of the molecules:

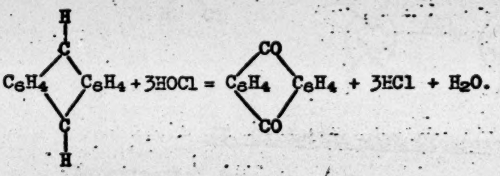
$$\overset{\curvearrowright}{H-O-H} \,.......\, \underset{+\delta}{Cl} \rightarrow \underset{-\delta}{Cl}$$

has been indicated previously by one of the authors [2].

The delaying effect of hydrochloric acid is to be explained by the displacement of the equilibrium of Equation 7 from right to left; the compound of the activated molecules, $\overset{\curvearrowright}{H - O - H} \,........\, \underset{+\delta}{Cl} \rightarrow \underset{-\delta}{Cl}$

is decomposed with formation of non-hydrated chlorine.

2. The oxidative process that is to be attributed to hypochlorous acid, which is formed by the hydrolysis of chlorine in accordance with Equation 7, proceeds by the following reaction:



(8)

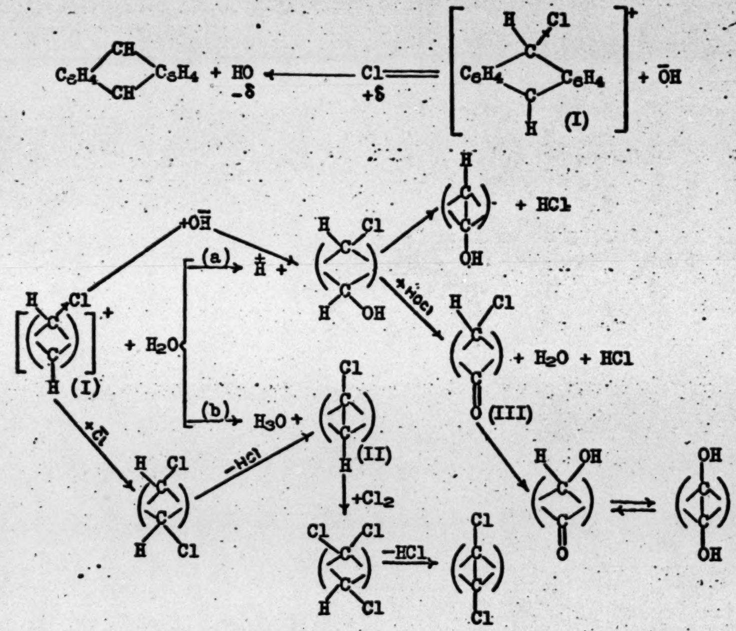
The hydrochloric acid that is formed in accordance with Equation 8 will clearly displace the equilibrium of Equation 7 from right to left, so that the concentration of hypochlorous acid will fall and reaction 8 will be slowed down. The equilibrium reaction 7 is the slowest of the reactions occurring and determines the order of the reaction.

The mechanisms of the reactions that explain the formation of the products indicated above may be formulated in the following way. As the meso carbons of anthracene are nucleophilic centers, they will be subject, above all, to the action of the halogen $\left(\underset{+\delta}{Cl}\right)$ which is poor in electrons, of the hypochlorous acid, with formation of the hypothetical cation (I), which can react with water according to (a) or (b), or can react with any anion in the solution.

The course of the successive reactions of anthracene with hypochlorous acid are shown in the diagrammatic scheme.

We have not succeeded in isolating, as reaction products, 9-chloroanthracene (II) and 9-chloroanthrone (III), but they are probably formed.

This interpretation of the oxidation of anthracene by means of chlorine water is in accord with the reactions of anthracene with bromine in aqueous acetone [9] and of olefins with hypochlorous acid [13].



II. Oxidation with Dichromate and Permanganate

Experimental Procedure. The determination of the rate of reaction of anthracene (9,10-dichloroanthracene) with dichromate or permanganate was carried out in a three-necked round-bottomed flask of 250 ml capacity with a reflux condenser. Through the condenser there passed a thermometer, a stirrer, and also a T-tube, in the side arm of which a glass rod was fixed by means of rubber tubing so that it held back a thin-walled test-tube containing the weighed amount of anthracene (9,10-dichloroanthracene). When the test-tube containing the sample had been placed in position on the rod, the upper end of the T-piece was closed with a stopper. The speed of stirring was kept constant (85-90 rev/min) in all experiments. Oxidizing agent, as a 0.1 N solution, was taken in known excess over the amount calculated according to the equation for the oxidation of anthracene (9,10-dichloroanthracene) to anthraquinone.

The test-tube containing the weighed amount of anthracene (or 9,10-dichloroanthracene), which had been mixed into a fine suspension with 4 ml of a 1% solution of sulfuric acid or with 4 ml of a 17.5% solution of caustic potash, was lowered, by withdrawing the rod, into 100 ml of the 0.1 N solution of the oxidizing agent, heated to boiling point (on a glycerol bath). The reaction was considered to start from that moment. After a definite interval of time, the solution was cooled rapidly and filtered. The amount of oxidizing agent remaining after the reaction was determined by iodometric titration.

The results of the experiments are given in Tables 8 and 9 and in Fig. 2.

It will be seen from Tables 8 and 9 and from Fig. 2 that, in the first place, the rate of oxidation of anthracene, both in acid and in alkaline medium, is notably higher than that of 9,10-dichloroanthracene and, in the second place, that the rate of oxidation of 9,10-dichloroanthracene is higher in alkaline medium than in acid medium. The latter fact leads us to assume that in the general chain of reactions from 9,10-dichloroanthracene to anthraquinone the oxidation reaction is preceded by the replacement of the halogens by hydroxyls with formation of 9,10-dihydroxyanthracene. 9,10-Dihydroxyanthracene appears to be an intermediate product also in the oxidation of anthracene. These considerations and also the fact that in oxidation reactions the meso carbon atoms of anthracene in taking up the configuration of anthraquinone lose three electrons, whereas 9,10-dichloroanthracene loses only one electron in the same process, lead one to assume the following scheme of changes:

TABLE 8

Oxidation by potassium dichromate in presence of sulfuric acid

Amount taken (g)	Time from start of expt. (min)	Amount of oxidizing agent taken (ml 0.1 N)	Amount of oxidizing agent used (ml 0.1 N)	Theor. required amt. of oxidizing agent (ml 0.1 N)	Amt. of oxidizing agent used as % of theor. reqd. amount	Remarks
			Anthracene			
0.2981	30	101.1	14.70	102.0	14.31	In all cases, 2 or 3 experiments were carried out for each period of time
0.2953	60	101.1	22.59	101.0	22.3	
0.2961	120	101.1	46.70	101.3	46.10	
0.2909	240	101.1	67.12	99.54	67.45	
			9,10-Dichloroanthracene			
0.4383	60	101.1	0.12	36.04	0.34	
0.4403	120	101.1	0.57	36.65	1.58	
0.4292	240	101.1	2.64	36.33	7.26	
0.4176	360	101.1	5.37	34.42	15.60	

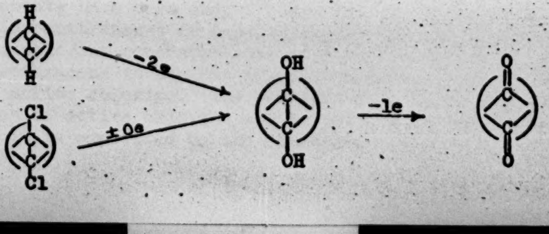


TABLE 9

Oxidation by potassium permanganate in alkaline solution

Amount taken (g)	Time from start of expt. (min)	Amount of oxidizing agent taken (ml 0.1 N)	Amount of oxidizing agent used (ml 0.1 N)	Theor. required amt of oxidizing agent (ml 0.1 N)	Amt. of oxidizing agent used as % of theor. reqd. amount	Remarks
			Anthracene			
0.1484	15	99.49	41.62	84.21	49.42	In all cases, 2 or 3 experiments were carried out for each period of time
0.1493	30	99.49	57.93	84.72	68.38	
0.1485	45	99.49	75.85	84.27	90.01	
0.1486	60	99.49	85.10	84.34	100.8	
			9,10-Dichloroanthracene			
0.6185	30	99.49	14.33	84.34	17.0	
0.6186	60	99.49	27.76	83.65	33.18	
0.6158	120	99.49	52.2	83.95	62.18	
0.6186	240	99.49	76.64	84.34	90.87	

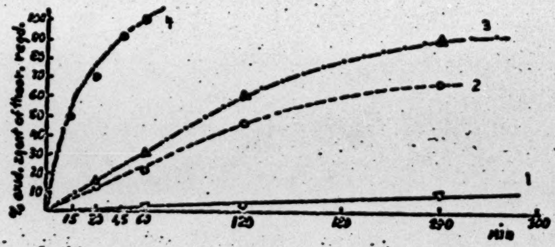


Fig. 2. Oxidation of anthracene (curves 2,4) and of 9,10-dichloroanthracene (1,3): 1) $K_2Cr_2O_7 + H_2SO_4aq$ (9,10-dichloroanthracene); 2) $K_2Cr_2O_7 + H_2SO_4aq$ (anthracene); 3) $KMnO_4 + KOHaq$ (9,10-dichloroanthracene); 4) $KMnO_4 + KOHaq$ (anthracene)

SUMMARY

1. Measurements have been made of the rate of the reaction between anthracene (9,10-dichloroanthracene) in aqueous suspension and chlorine at 2-3° and at 15-16°, using chlorine concentrations of 0.01 N and 0.05 N. The oxidation by chlorine of anthracene in aqueous suspension proceeds as a first-order reaction with respect to active chlorine. The reaction rate increases with increase in the concentration of active chlorine and is reduced by the hydrochloric acid that is formed; it is expressed by the equation:

$$-\frac{d[Cl_2]}{dt} = k'_2 \frac{[Cl_2]}{[HCl]}$$

2. It has been shown that the rate of oxidation of anthracene by chlorine water falls sharply towards the end owing to the formation of 9,10-dichloroanthracene, for the rate of the oxidation of the latter is many times less than the rate of the anthracene reaction.

3. The products of the oxidation of anthracene by aqueous chlorine at 15-16° for 60 hr have been isolated and identified. They are: anthraquinone (62%), 9,10-dihydroxyanthracene and oxanthranol (7%), 9-hydroxyanthracene (3%), 9,10-dichloroanthracene (12%), and unchanged anthracene (13%).

4. The mechanism of the oxidation of anthracene by aqueous chlorine has been indicated.

5. Measurements have been made of the rate of oxidation of anthracene and of 9,10-dichloroanthracene by the oxidizing agents: $K_2Cr_2O_7 + H_2SO_4aq$ and $KMnO_4 + KOHaq$.

It has been shown: 1) that the rate of oxidation of anthracene, both in acid and in alkaline solution, is many times higher than the rate of oxidation of 9,10-dichloroanthracene, and 2) that the rate of oxidation in alkaline medium is 4 to 5 times higher than in acid medium in the case of anthracene and is 60 to 80 times higher in the case of 9,10-dichloroanthracene.

Institute of Organic Chemistry
of the U.S.S.R. Academy of Sciences

Received April 16, 1951

LITERATURE

1. B.P. Federov. Bull. Acad. Sci. U.S.S.R. Div. Chem. Sci., 5, 582 (1951).

2. B.P. Federov and V. Semenova. J. Appl. Chem. 13, 1076 (1940).

3. B.P. Federov. Bull. Acad. Sci. U.S.S.R. Div. Chem. Sci., 3, 309 (1947).

4. A. Yakovkin. J. Russ. Phys. Chem. Soc., 32, 673 (1900).

5. K. Meyer. Ann. 379, 37-73 (1911); Germ. Pat. 250075 (281910).

6. K. Meyer, Zahn, Ann. 396, 166 (1913).

7. E. Plazek, from C. 1931, I, 1427; Roczniki Chem. 10, 761 (1930).

8. G. Charrier, G. Grippa, Gaz. chim. ital. 57, 741 (1927).

9. Ch. Price, C. Weaver, J. Am. Chem. Soc. 61, 3360 (1939).

10. Liebermann, Ann. 212, 6 (1882).

11. E.A. Shilov. Cotton Ind., No. 1, 36 (1937); Bull. Text. Res. Inst. of Ivanovo-Voznesensk, No. 4/5 (1933).

12. E.A. Shilov, N. Konyaev, and A. Otmennikova. J. Phys. Chem. 8, 909 (936); 10, 123 (1937); 19, 405 (1945).

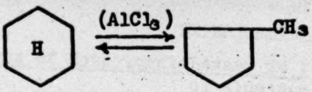
13. R. Norris, R. Vogt, G. Hennion, J. Am. Chem. Soc. 61, 1458, 1460 (1939); C. Irvin, G. Hennion, J. Am. Chem. Soc. 63, 858 (1941). P. De la Marl, E. Hughes, C. Vernon, Research (Lond.) 3, 242 (1950); from C. A. 44, 7751 (1950).

BLANK
PAGE

REACTIONS OF METHYLCYCLOHEXANE AND TOLUENE IN CONTACT WITH ALUMINUM CHLORIDE

N. I. Shuykin and L. M. Feofanova

The isomerization of cycloalkanes, particularly the conversion of one ring into another, under the action of anhydrous aluminum bromide or chloride has been studied over a long period by Zelinsky and his coworkers [1], and also by some foreign authors [2]. A number of investigators have noted that reactions of another type occur at the same time; these consist in the transference of methyl side groups from one ring to another. Thus there are indications that the isomerization of cyclohexane into methylcyclopentane in presence of aluminum chloride:



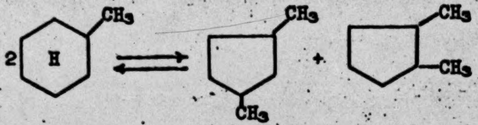
which has been studied over a range of temperatures and pressures, is accompanied by the formation of a certain amount of 1,3-dimethylcyclohexane [3].

An analogous process consisting in the redistribution of methyl groups among molecules under the action of aluminum chloride is observed also in the reactions of xylene [4]. One of us has shown [5] that when aluminum chloride acts upon an equimolecular mixture of xylene and benzene at 250-300° a redistribution of methyl groups occurs with formation of toluene:

$$C_6H_4(CH_3)_2 + C_6H_6 \rightarrow 2C_6H_5CH_3.$$

In this connection it appeared to be of interest to determine the behavior of the simplest homolog of benzene, toluene, and also of methylcyclohexane, in contact with anhydrous aluminium chloride at a comparatively low temperature (80°), i.e. under conditions that preclude, on the one hand, the occurrence of cracking and, on the other hand, the formation of more complex polycyclic systems. In the investigation of the behavior of methylcyclohexane under these mild conditions it was of interest to determine whether in addition to dimethylcyclopentanes - the possible products of the isomerization of methylcyclohexane with shrinkage of the ring - dimethylcyclohexanes are formed.

In the experiments with toluene, the determination of the possibility of the formation of benzene and xylene under the selected conditions was of special interest. The main experiments were carried out with fairly large amounts (400 g of each) of methylcyclohexane and toluene, and it was therefore possible, by the aid of precise rectification, to identify all the products of the possible reactions, even when they were formed in small amount. Investigation of the reaction products showed that the main reaction of methylcyclohexane in presence of aluminum chloride at 80° is isomerization with shrinkage of the ring into dimethylcyclopentanes (mixture of 1,3- and 1,2 isomers):



This equilibrium stands very much on the left side under our conditions, for only about 2-5%, depending on the time of contact with $AlCl_3$, of the methylcyclohexane taken is converted into dimethylcyclopentanes. Transalkylation, i.e. the redistribution of methyl groups, occurs to an insignificant extent: only very small amounts of cyclohexane and dimethylcyclohexane could be found among the reaction products. When toluene is brought into contact with aluminum chloride under analogous conditions, redistribution of methyl groups is more in evidence. Among the reaction products there were found, in addition to the main mass of unchanged toluene, benzene and all the isomeric xylenes, with a predominance of m-xylene, in appreciable amounts:

$$2C_6H_5CH_3 \underset{}{\overset{AlCl_3}{\rightleftarrows}} C_6H_6 + C_6H_4\cdot(CH_3)_2.$$

EXPERIMENTAL

Reactions of Methylcyclohexane in the Liquid Phase in Presence of Aluminum Chloride

Pure synthetic methylcyclohexane, b.p. 99.8° at 736 mm, n_D^{20} 1.4225 and d_4^{20} 0.7692, was taken for the experiments. The reaction was carried out in a three-necked flask provided with a mechanical stirrer and a long reflux condenser with a calcium chloride tube. The temperature of the reaction mixture was maintained at 80° by means of an oil-bath.

The time of the treatment of methylcyclohexane in contact with aluminum chloride varied from 4 to 24 hr. In different experiments the amount of aluminum chloride was varied over the range 4 to 20% on the weight of methylcyclohexane taken. Two series of experiments were carried out. The conditions employed in the first series are shown in Table 1. In no case was the evolution of gaseous products observed; the hydrocarbon and the aluminum chloride did not change appreciably in color.

TABLE 1

Conditions employed in the first series of experiments with methylcyclohexane

No. of expt.	Amt. of methylcyclohexane taken (g)	Amt. of aluminum chloride taken (%)	Duration of experiment (hr)	Amount of catalyzate obtained	
				(g)	(%)
1	490	4	4	472.5	96.4
2	100	4	8	94.0	94.0
3	220	4	20	206.6	93.9
4	70	8	4	66.0	94.3

At the end of the reaction the hydrocarbon layer was poured off from the aluminum chloride and washed in a separating funnel, first with a 10% solution of caustic soda and then with water; it was dried over calcium chloride. The refractive indices of the catalyzates obtained varied inappreciably (1.4230-1.4238) and differed little from the refractive index of the original methylcyclohexane. All the catalyzates were fractionally distilled using a column with a metal filling and with an efficiency of 28 theoretical plates. Independently of the conditions under which the experiments were carried out, they all yielded fractions boiling in the range 88-100° at 752 mm. The corresponding fractions (88-95°, 95-98°, 98-99° and 99-100°) of the catalyzates from all the four experiments were united and again fractionally distilled in the same column.

The results obtained are given in Table 2.

TABLE 2

Results of the Second Fractionation at 750 mm of the Fractions Obtained from the Catalyzates of the First Series of Experiments[1]

Fraction No.	Boiling point (°C)	Amount (g)	n_D^{20}	d_4^{20}	Yield of fraction (% of united catalyzates)
1	80.5-90	4.6	1.4125	0.7538	0.56
2	90-91	12.5	1.4100	0.7507	1.54
3	91-95	8.6	1.4145	0.7565	1.00
4	95-98	18.8	1.4220	0.7602	2.30
5	98-99	28.5	1.4228	0.7680	3.50
6	99-100.2	713.8	1.4235	0.7691	87.90
	Residue	25.5			3.10

---

[1] For the second fractionation, in all 837.0 g of the separate fractions of the catalyzates was taken.

The residue (25.5 g) obtained in the second distillation of the catalyzate fractions, on subsequently distilling over sodium (745 mm), came over within the range 99.5-100°. The new small residue (about 2 g) was a dark-brown resinous mass.

As will be seen from Table 2, the first 3 fractions do not differ essentially in their properties from the original methylcyclohexane. Judging from its initial boiling point, fraction 1 may contain a certain amount of cyclohexane together with possible dimethylcyclopentanes.

Fraction 2 (90-91°) is very close in its properties to 1,3- and 1,2-dimethylcyclopentanes. Thus Zelinsky [6] gives the following constants for 1,3-dimethylcyclopentane: b.p. 90.6-90.8°; n_D^{20} 1.4096; d_4^{20} 0.7543; 1,2-dimethylcyclopentane, according to Chavanne [7], has: b.p. 90.95° at 741 mm, n_D^{20} 1.4093 and d_4^{20} 0.75137.

Fraction 3, evidently, is an intermediate one; it was not investigated further.

In order to elucidate the chemical nature of the hydrocarbons entering into the composition of these fractions, they were subjected to Zelinsky's catalytic dehydrogenation treatment. Platinized silca gel was used as catalyst (10% Pt). Each fraction was passed 2 to 3 times over the catalyst at 300-305° until the refractive index did not change further. After the aromatic hydrocarbons in the catalyzates formed had been estimated, they were removed by means of sulfonation. Fractions 1 and 2 were then again isomerized in presence of aluminum chloride. The isomerates obtained, after suitable treatment, were dehydrogenated over the same catalyst. The results of the investigation of the first four fractions separated from the united isomerizate are given in Table 3.

TABLE 3

Investigation of the Products of the Reaction of Methylcyclohexane in Contact with Aluminum Chloride (First Series of Experiments)

Fraction No.	Properties of the original fraction			Properties of fraction after dehydrogenation		
	Boiling range, °C	n_D^{20}	d_4^{20}	n_D^{20}	d_4^{20}	Content of aromatic hydrocarbons (%)
1	80.5-90	1.4125	0.7538	1.4160	-	3.3
2	90-91	1.4100	0.7507	1.4105	0.7498	Traces
3	91-95	1.4145	0.7565	(a)1.4235	-	
				(b)1.4335	-	28.3
				(c)1.4345	-	
4	95-98	1.4220	0.7602	(a)1.4495	-	
				(b)1.4650	-	
				(c)1.4770	-	
				(d)1.4935	-	94.0

As will be seen from this table, on passing the 80.5-90° fraction over Pt-silica-gel, its refractive index changes to an insignificant extent. There was 3.3% of aromatic hydrocarbons, evidently benzene, in the catalyzate. The benzene would be formed from cyclohexane, which could arise from methyl-group transfer among methylcyclohexane molecules. Owing to the insignificant amount of this fraction, we did not succeed in separating and identifying benzene.

It will be seen also from Table 3 that the refractive index of the 90-91° fraction remained practically unchanged after dehydrogenation. In the catalyzate obtained, no aromatic hydrocarbons could be detected. In order to confirm the natural supposition that this fraction contains mainly cyclopentane derivatives, the catalyzate obtained was isomerized in presence of $AlCl_3$ at 80° and then catalytically dehydrogenated at 300°. The results of the estimation of aromatic hydrocarbons in the condensate obtained confirmed our supposition.

After repeating the catalytic dehydrogenation of fraction 3 (91-95°) three times, a condensate containing 28.3% of toluene was obtained, which points to the presence in the fraction of about 30% of unchanged methylcyclohexane. After the dehydrogenation of fraction 4 (95-98°), 94% of aromatic hydrocarbons was found in the catalyzate. It therefore follows that this fraction is almost unchanged methylcyclohexane.

Reactions of Methylcyclohexane in Presence of an Increased Amount (to 20%) of Aluminium Chloride

The second group of experiments with methylcyclohexane was carried out in the same apparatus under conditions analogous to those used in the first series of experiments, apart from the amount of $AlCl_3$ taken, which was 20% of the weight

TABLE 3 (Continued)

Investigation of the Products of the Reaction of Methylcyclohexane in Contact with Aluminum Chloride (First Series of Experiments)

Properties of the catalyzate after removal of aromatics		Properties of the catalyzate freed from aromatics and then isomerized over $AlCl_3$		Properties of the isomerizate after dehydrogenation		Properties of the aromatic-free residue	
n_D^{20}	d_4^{20}	n_D^{20}	d_4^{20}	n_D^{20}	Content of aromatics, %	n_D^{20}	d_4^{20}
1.4117	0.7531	1.4140	0.7568	1.4170	15.0	1.4080	0.7460
1.4095	0.7496	1.4210	0.7660	(a)1.4680			
				(b)1.4870	87.0	1.4090	0.7492
1.4115	0.7492	1.4190	-				
1.4175	-	-					

TABLE 4

Results of the Second Fractionation (at 755 mm) of the United Fractions of the Catalyzates of the Second Group of Experiments

Fraction No.	Boiling range (°C)	Amount (g)	n_D^{20}	d_4^{20}	Yield of fraction	
					On original methylcyclohexane	On the total products of the second distillation
1	82-87	4.4	1.4050	0.7515	0.6	0.7
2	87-89	26.2	1.4113	0.7499	3.3	3.9
3	89-91	10.5	1.4105	0.7504	1.3	1.6
4	91-98	20.0	1.4210	0.7660	2.5	3.0
5	98-99	35.0	1.4229	0.7683	4.4	5.2
6	99-100.2	568.0	1.4230	0.7692	72.0	85.2
7	124-131	2.4	1.4230	0.7606	0.30	0.4

of hydrocarbon taken, and the duration of the reaction, which was increased to 24 hr. Two experiments were carried out in which methylcyclohexane was treated with $AlCl_3$ under completely identical conditions. In the first of these (No.5), 400 g of methyclcyclohexane was taken, in the second, 390 g. The two isomerizates obtained were first distilled separately through the same column of 28 theoretical plates. Fractions boiling within the range 82-100° at 755 mm were separated.

Fractions boiling in identical ranges (82-87; 87-89; 89-91; 91-98; 98-99°) were then united and again fractionated through the same column. The results obtained in the second distillation are given in Table 4.

Fractions 1, 2, and 7 were catalytically dehydrogenated at 300° (see Table 5). The contents of aromatic hydrocarbons in the catalyzates obtained were determined by the sulfuric acid method. In the catalyzate of fraction 1 (82-87°), 19% of aromatic hydrocarbons was found. According to its constants, the residue of this fraction after freeing from aromatics was 1,3-dimethylcyclopentane.

After fraction 2 (87-89°) had been passed over platinized silica gel, its refractive index suffered an inappreciable change, which gives us reason to consider that it consists mainly of dimethylcyclopentanes; its physicochemical properties are in accord with this view.

In order to elucidate the nature of fraction 7 (124-131°), having n_D^{20} 1.4230 and d_4^{20} 0.7606, it was subjected to catalytic dehydrogenation. After two passages over Pt – silica-gel, a catalyzate having n_D^{20} 1.4933 and d_4^{20} 0.8623 was obtained. Fractional distillation of this catalyzate at 740 mm yields the fractions:

Fr. 1, b.p. 111-116° – 0.21 g;
Fr. 2, b.p. 117-135° – 0.24 g.

Both fractions were oxidized by Ullmann's method [8].

TABLE 5

Investigation of the Products of the Reaction of Methylcyclohexane in Presence of 20% $AlCl_3$

Fraction No.	Boiling range (°C)	n_D^{20}	d_4^{20}	After dehydrogenation			Properties of the catalyzate after removal of aromatics	
				n_D^{20}	d_4^{20}	Content of aromatics (%)	n_D^{20}	d_4^{20}
1	82-87	1.4050	0.7515	1.4145	–	19.0	1.4035	0.7452
2	87-89	1.4113	0.7499	1.4118	–	2.0	1.4087	0.7482
7	124-131	1.4230	0.7606	(a)1.4898	–			
				(b)1.4933	0.8623			

The separation of the acids obtained was carried out by the method described by Moldavsky, Kamusher, and Kobylskaya [9]. As a result of the oxidation of the 111-116° fraction, benzoic acid, m.p. 121°, was obtained. From the products of the oxidation of the 117-135° fraction, after separation of benzoic acid, the methyl ester of isophthalic acid [9], m.p. 62-64°, was obtained. The presence of isophthalic acid in the oxidation products of this fraction indicates the presence of m-xylene in the catalyzate. The m-xylene is evidently formed as a result of the methyl-redistribution reaction of methylcyclohexane in presence of aluminium chloride.

Reactions of Toluene in the Liquid Phase in Presence of Aluminum Chloride

In the experiments with toluene, the question of the possibility of the formation of benzene and xylene in presence of aluminum chloride under our conditions was of fundamental interest. The toluene taken for the experiments was first distilled through a column (see above); it had the following properties: b.p. 109.5-110° at 750 mm; n_D^{20} 1.4965; d_4^{20} 0.8666.

The reaction was carried out under the conditions used for methylcyclohexane, the time in contact with aluminum chloride being 8 hr. In different experiments the amount of aluminum chloride was varied from 4 to 10% on the weight of toluene taken.

As it was found that the catalyzates obtained by the use of various amounts of $AlCl_3$ did not differ essentially from one another, they were all united for further investigation. In no experiment was the evolution of gaseous products observed. The color of the hydrocarbon did not change appreciably, but a small amount of a dark-colored resin-like layer was formed on the bottom of the flask. 1426 g of toluene was treated in three batches with aluminum chloride. 1123 g of a hydrocarbon layer and 338 g of a toluene - aluminum chloride complex were isolated. The hydrocarbon layer, after being washed and dried with calcium chloride, was fractionated over sodium through the column at 752 mm. Three fractions were separated; their properties are given in Table 6.

TABLE 6

Results of the Action of $AlCl_3$ on Toluene

No. of fraction	Boiling range (°C)	n_D^{20}	d_4^{20}	Weight (g)	Yield of fraction (%)	
					On original toluene	On isomerizate obtained
1	80-108	1.4980	0.8724	18.8	1.3	1.7
2	108-110	1.4965	0.8666	948.0	66.5	84.4
3	110-141	1.4975	0.8683	56.0	4.0	5.0

Fraction 1 (80-108°) was again fractionated under the same conditions; 12.5 g of benzene, b.p. 79.5-80° at 753 mm; n_D^{20} 1.4995; d_4^{20} 0.8755, was isolated from this fraction.

The properties of Fraction 2 indicate it to be almost unchanged toluene (108-111°). Fraction 3 (110-141°) was separated by fractionation through the column into five fractions, the properties of which are given in Table 7.

The data in Table 7 show that, as a result of further fractionation of the 110-141° distillate, xylene fractions boiling over the range 136-141° have been separated; the total quantity of these (without the residue) was 29.3 g, or about 2%, calculated on the original toluene. In order to determine the structures of the xylenes, the fractions obtained (136-139°, 139-141°, and also the part boiling at 141°) were oxidized by Ullmann's method [8]. The relative amounts of isomers in each fraction was established by separation of the acids obtained by oxidizing that particular fraction. The separation of the acids was carried out by the method described by Moldavsky and coworkers [9]. The results of the analysis of the oxidation products are presented in Table 8.

It follows from the results given in Table 8 that the 136-139° fraction consists essentially of m-xylene, the 139-141° fraction contains a considerable

TABLE 7

Results of the Refractionation of the 110-141° Fraction

No. of fraction	Boiling range (°C at 756 mm)	Amount (g)	n_D^{20}	d_4^{20}
1	107.5-109.5	20.4	1.4955	0.8655
2	126-136	1.3	1.4960	0.8650
3	136-139	16.9	1.4965	0.8656
4	139-141	3.9	1.5000	0.8704
5	141	8.5	1.5010	0.8855
	Residue	3.0		

TABLE 8

Results of the Analysis of the Oxidation Products of the Xylene Fractions

Boiling range of fraction	Amounts of the acids obtained (% of total quantity of oxidation products)			
	Benzoic	Phthalic	Isophthalic	Terephthalic
136-139	0.5	3.4	82.5	13.6
139-141	0.4	29.8	63.2	6.6
141	-	75.7	19.0	5.3

amount of m-xylene (63.2%) together with appreciable amounts of o- and p-xylenes, and the part of the catalyzate boiling at 141° consists mainly of o-xylene, though even here there is appreciable admixture with m-xylene.

SUMMARY

1. A study has been made of the reactions of methylcyclohexane in the liquid phase in presence of anhydrous aluminum chloride at 80° under normal pressure.

2. It has been established that when methylcyclohexane reacts with aluminum chloride under these conditions it not only isomerizes with shrinkage of the ring into dimethylcyclopentane, but also undergoes the process of methyl-group redistribution to a small extent and, as a result, dimethylcyclohexane and cyclohexane are formed.

3. It has been shown that in the reaction of aluminum chloride with toluene under analogous conditions there is a redistribution of methyl groups resulting in the formation of benzene and a mixture of isomeric xylenes.

Institute of Organic Chemistry
of the USSR Academy of Sciences

Received April 14, 1951

LITERATURE CITED

[1] N.D.Zelinsky and I.Pappe. J.Russ.Chem.Soc., 37, 625 (1905); M.B.Turova-Polyak and coworkers. J.Gen.Chem., 9, 233, 429, 1279, 2179 (1939); 10, 172, 1435 (1940); N.D.Zelinsky, M.B.Turova-Polyak, and G.R.Gasan-Zade. Proc.Acad.Sci.USSR, 32, 8, 550 (1941); M.B.Turova-Polyak and coworkers. J.Gen.Chem., 11, 817, 824 (1941); 13, 353 (1943); 14, 337 (1944); 16, 825, 829 (1946); 17, 137 (1947); 18, 179 (1948); Proc.Acad.Sci.USSR, 60, 5, 807 (1948).

[2] O.Aschan. Ann., 324, 10 (1902); C.D.Nenitzescu and J.P.Cantuniari. Ber., 66, 7-9, 1097-1100 (1933); V.Grignard and R.Stratford. Comptes rend., 178, 2143 (1924).

[3] V.N.Ipatev and V.I.Komarevsky. J.Am.Chem.Soc., 56, 1926 (1934); L.Glasebrook and W.W.G.Lovell. J.Am.Chem.Soc., 61, 1717 (1939); see Yu.A.Arbuzov and N.D. Zelinsky, Proc.Acad.Sci.USSR, 23, 793 (1939).

[4] R.Anschutz and H.Immendorf. Ber., 17, 2816 (1884); 18, 659 (1885); O.Jacobsen. Ber., 18, 338 (1885); R.Heiseu and A.Tohl. Ann., 270, 155 (1892); F.Fischer and H.Niggeman. Ber., 49, 1475 (1916); I.F.Norris and G.T.Vaala. J.Am.Chem.Soc., 61, 2131 (1939).

[5] N.I.Shuykin and M.S.Prokhorova. J.Gen.Chem, 16, 835 (1946).

[6] N.D.Zelinsky. Ber., 30, 387 (1897).

[7] G.Chavanne. Bull.soc.chim.Belg., 39, 402 (1930).

[8] F.Ullmann. Ber., 36, 1798 (1903).

[9] B.L.Moldavsky, G.D.Kamusher, and M.V.Kobylskaya. J.Gen.Chem., 7, 167 (1937).

THE CATALYTIC HYDROCONDENSATION OF CARBON MONOXIDE WITH OLEFINS

COMMUNICATION 7. EFFECT OF THE CARBON MONOXIDE CONCENTRATION ON THE HYDROCONDENSATION REACTIONS OF CARBON MONOXIDE WITH PROPENE AND WITH n-BUTENE

Ya. T. Eydus, N. D. Zelinsky, K. V. Puzitsky, and N. I. Ershov

We have previously shown that equimolecular mixtures of n-butene and hydrogen [1], propene and hydrogen [2], and ethylene and hydrogen [3], containing 4-7% of carbon monoxide, undergo catalytic hydrocondensation with formation of a liquid product that consists of saturated aliphatic hydrocarbons and olefins. For an ethylene-hydrogen mixture it was shown that this reaction does not occur in the complete absence of carbon monoxide in the original gas mixture, the ethylene being then hydrogenated to ethane. An ethylene-hydrogen mixture containing 15% of carbon monoxide, e.g. $1CO:2H_2:3C_2H_4$, undergoes also the hydrocondensation reaction [4]. About 80% of the original ethylene participates in the formation of the condensate, and 20% is hydrogenated to ethane. The liquid condensate, which is essentially a mixture of aliphatic hydrocarbons, contains a small admixture of organic compounds containing oxygen [5].

EXPERIMENTAL

The present work has as its object the investigation of the effect of the carbon monoxide concentration on the hydrocondensation reactions of carbon monoxide with propene and with n-butene. The apparatus, procedure, and experimental conditions, and also the preparation, purification, and analysis of the gases, were the same as in the previous work [1,2]. For the preparation of the initial gas mixtures, 95% propene, prepared by the dehydration over aluminum oxide of isopropyl alcohol, b.p. 81-81.5°; d_4^{20} 0.7898; n_D^{20} 13779; Found MR_D 17.53; calculated MR_D 17.58, was used. After condensation, this propylene was redistilled through a Davis column over the range -46.5 to -45°. The butene used in the experiments was prepared from n-butyl alcohol as in the previous work [1].

The Experimental Results and their Discussion

1. Experiments with propene. Experiments, analogous to those carried out with ethylene [3], were directed to the study of the dependence of the degree of polymerizability of the propene-hydrogen mixture on the carbon monoxide concentration, which varied over the range 0-22% of the initial gas mixture. The results are given in Tables 1, 2 and 3.

The experiments were carried out over freshly reduced catalysts 21, 22, 23, 24, 25, 26, 27 and 28 with a space velocity of 80-100 liter/liter hr.

Experiment 148 (Table 1) was carried out with a gas mixture prepared from propene that had been twice condensed at -70° with removal of the gaseous residue by pumping, then passed in the gaseous condition, after the usual purification, through three columns containing ammoniacal cuprous chloride, the gas being forced through the Schott filters in the bases of the columns. This was done with the aim of freeing the gas completely from carbon monoxide, which may be formed as a by-product during the dehydration of the alcohol, owing to decomposition of the aldehyde. Actually, the amount of carbon monoxide in the initial gas of Experiment 148 was nil with a possible error of 0.05%, the method of estimation being more accurate than the usual gas-analysis method. In this experiment, as also in Experiment 149, in which a gas mixture containing 0.2% of carbon monoxide was used, the yield of heavy oil was nil and that of light oil extremely small (20-27 ml/m^3, or 1.4-1.8

TABLE 1

Catalyst	Expt. No.	Duration of expt., hours	CO in initial mixture, %	Volume ratio C_3H_6:H_2 in initial mixture	Contraction, %	Yield (ml/m^3) of heavy oil (H)	Yield (ml/m^3) of light oil (L)	Yield (ml/m^3) of oil (H + L)	Volume ratio H/L	Yield of oil (H + L) ml/liter per hour
22	148	12.0	0.0	1.0	51.2	0.0	27.0	27.0	0.0	1.8
22	149	12.0	0.2	1.0	44.2	0.0	20.5	20.5	0.0	1.4
22	150	6.0	1.3	1.0	51.0	12.0	84.0	96.0	0.14	6.5
23	152	5.0	1.8	1.1	47.0	32.1	128.4	160.5	0.25	12.5
24	153	6.0	2.0	0.9	50.5	23.9	161.7	185.6	0.15	12.3
22	151	6.0	2.8	1.0	44.0	40.0	131.6	171.6	0.30	11.9
26	155	6.0	3.7	1.4	52.4	43.6	217.8	261.4	0.20	26.6
25	154	6.0	3.7	1.1	47.4	97.7	293.1	390.8	0.33	29.4
21	147	12.0	5.7	1.1	66.4	239.8	337.7	577.5	0.71	35.5
21	144	11.2	6.2	0.9	69.5	277.4	275.1	552.5	1.01	36.1
27	156	6.0	11.6	1.6	52.2	216.5	97.0	313.5	2.23	30.6
28	161	5.0	13.6	1.5	44.8	125.4	66.0	191.4	1.90	19.7
27	157	6.0	14.2	1.2	39.0	102.3	40.1	142.4	2.55	13.0
27	158	6.0	15.4	1.4	32.9	85.8	18.5	104.3	4.63	10.6
28	160	6.0	18.4	1.8	40.2	98.2	30.5	128.7	3.22	11.7
28	159	6.0	22.0	1.9	38.5	82.5	29.7	112.2	2.78	10.6

TABLE 2

Expt. No.	Composition of initial gas (vol.%)[1]				Composition of effluent gas (vol. %)[2]				
	C_3H_6	H_2	CO	N_2	C_3H_6	H_2	CO	C_3H_8	N_2
155	53.2	36.0	3.7	7.0	45.8	8.8	0.0	32.3	13.0
147	47.3	43.2	5.7	2.8	17.8	7.1	1.3	57.1	15.2
144	42.2	46.6	6.2	4.6	0.5	1.4	0.5	72.6	23.9
156	49.6	30.9	11.6	6.0	62.4	7.6	1.8	16.5	7.3
161	49.4	30.2	13.6	3.5	66.4	9.0	7.2	9.9	6.5
157	43.0	36.6	14.2	4.8	58.4	15.6	8.4	7.8	8.2
158	46.2	32.3	15.4	5.0	58.8	17.0	11.6	4.6	6.4
160	48.0	26.5	18.4	5.5	66.4	6.6	13.0	5.7	6.1
159	48.0	25.0	22.0	3.9	65.2	4.4	15.4	5.7	5.5

---

[1]) The defect from 100% must be regarded as oxygen.

[2]) The defect from 100% must be regarded as oxygen and carbon dioxide, the combined content of which attained 2-3% in some of the gases.

TABLE 3

No. of experiment	CO in initial gas (%)	Amount that reacts (%)			Ratio of the reacting volumes of	
		C_3H_6	H_2	CO	H_2 and CO (H_2/CO)	C_3H_6 and CO (C_3H_6/CO)
155	3.7	60.3	88.7	100.0	7.7	8.7
147	5.7	87.5	90.3	92.6	7.4	7.9
144	6.2	99.7	99.1	97.0	9.7	9.1
156	11.6	39.3	88.3	91.1	2.5	1.8
161	13.6	26.0	84.6	70.9	2.7	1.3
157	14.2	17.0	74.0	63.9	2.9	0.8
158	15.4	14.5	64.7	49.2	2.7	0.8
160	18.4	17.3	85.4	58.0	2.1	0.7
159	22.0	16.2	89.0	57.0	1.8	0.6

ml/liter hour, to 577.5 ml/m^3, . or 36.1 ml/liter hour, also the volume ratio of heavy to light oil increases from 0.0 to 1.0, which also indicates an increased degree of condensability with increase in carbon monoxide concentration. An analogous relation is observed also for the % of propene that has reacted; this rises from 60.3 to 99.7 when the carbon monoxide concentration rises from 3.7 to 6.2% (Table 3).

With further increase in the carbon monoxide concentration, the yield of liquid condensate and the % of propene that has reacted begin to fall sharply, and at 14% CO and higher they remain constant at a fairly low level: 10.6-13 ml/liter hour for the yield of oil and 14.5-17.3% for the amount of propene that has reacted. Thus, in contrast to ethylene [4,5], propene does not undergo the hydrocondensation reaction with carbon monoxide when the content of the latter is equal to or in excess of 14-15%. In Figure 1 these relationships are shown graphically (Curves a and b).

It will be seen from Table 3 and Figure 1 (Curve c) that the ratios of the reacting volumes of the components, C_3H_6/CO and H_2/CO, are quite different in the regions of high and of low carbon monoxide concentration. In the low-concentration region (up to 6%), these quantities have the values 7.9-9.1 and 7.4-9.7 respectively, i.e., on the average 8-9. At carbon monoxide concentrations of 14% and greater, the values fall sharply to 0.6-1.8 and 1.8-2.9 respectively. It will be seen from Table 1 that a certain degree of variability in the initial volume ratio C_3H_6/H_2 has no appreciable effect on the way in which the process is found to depend on the carbon monoxide concentration.

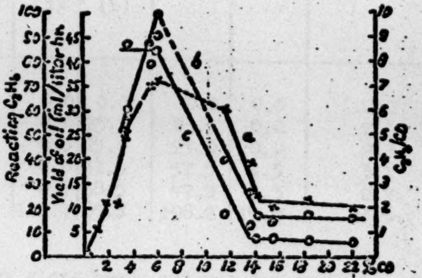


Fig. 1

The fraction of reacting hydrogen remains almost independent of the carbon monoxide concentration and has the value of 85-99%. Only for a carbon monoxide concentration of 14-15% does the fraction of reacting hydrogen fall somewhat (to

65-74%). As regards the amount of reacting carbon monoxide, this falls continuously as the CO concentration increases, but in absolute amount, carbon monoxide reacts to an extent that is 1.5-2 times greater in regions of high concentration than in regions of low concentration. This is deduced from a comparison in various experiments of the product obtained by multiplying the fraction of carbon monoxide in the initial gas mixture by the fraction of reacting carbon monoxide in the same experiment.

It is evident from the results obtained that completely different processes occur in the regions of low and of high carbon monoxide concentration. In the first case, propene undergoes the processes of hydrocondensation with carbon monoxide and of hydropolymerization, and these become more intense as the carbon monoxide content of the mixture increases. Here there is a manifest resemblance between propene and ethylene. In the second case this process is suppressed; less than 15% of the original propene takes part in it. The main reaction is between carbon monoxide and hydrogen, evidenced by the yield of oil, 110-140 ml/m^3 or 10-13 ml/liter hour, and, particularly, by the ratio of the reacting volumes of hydrogen and carbon monoxide (H_2/CO = about 2). Here we already find a difference between the behavior of propene on the one hand and of ethylene on the other, for the latter very readily undergoes hydrocondensation with carbon monoxide when the content of the latter in the initial mixture is high [4,5]. This difference is evidently determined by the existence of adsorption and steric difficulties in the case of propene.

2. Experiments with n-Butene. In Table 4 the results are given of experiments on the hydrocondensation of an equimolecular mixture of n-butene and hydrogen in absence of carbon monoxide at 190° under atmospheric pressure.

TABLE 4

Catalyst	Experiment No.	Duration of experiment, hours	Space velocity, liter/liter hour	CO in original gas (%)	Contraction (%)	Yield (ml/m^3)				Yield of oil (H + L, in ml/liter hr)
						Heavy oil (H)	Light oil (L)	H + L	Water	
Glass beads	173	4.0	94	0.0	0.0	0.0	0.0	0.0	0.0	0.0
34	171	5.5	90	0.00	57.1	0.0	23.5	23.5	0.0	2.0
34	172	6.0	100	0.00	56.2	0.0	25.9	25.9	0.0	2.3
35	174	24	60	0.0	47	6.0	51.5	57.5	4.5	3.1
35	175	12	68	0.0	55	8.7	38.5	47.2	5.3	2.7
35	176	10.7	75	2.5	53	112.7	85.5	198.2	15.0	13.5

Experiment 173 was carried out over glass beads and was for control purposes. The remaining experiments were carried out over freshly reduced catalysts 34 and 35.

It will be seen from Table 4 that in absence of carbon monoxide the hydrocondensation of n-butene does not occur to an appreciable extent. Experiments 171 and 172 were carried out with mixtures containing butene that had been carefully purified from carbon monoxide by liquefying it several times and pumping off the unliquefied gaseous residue on each occasion. In these experiments the yield of oil was 24-26 ml/m^3, and no heavy oil was obtained. In Experiments 173 and 174 the original butene was not specially purified from carbon monoxide, and

TABLE 5.

Catalyst	Experiment No.	Duration of exp. (hr)	Space velocity (liter/liter hour)	CO in original gas (%)	Vol. ratio C_4H_8/H_2 in initial gas	Contraction (%)	Yield (ml/m^3)				Yield of oil (H + L, in ml/liter hour)	Vol. ratio H/L
							Heavy oil (H)	Light oil (L)	H + L	Water		
36	177	6	86	5.8	0.85	61.1	106.1	283.2	389.3	28.3	30.5	0.37
36	178	5	97	5.5	0.98	67.1	158.6	377.6	536.2	37.7	48.0	0.42
36	179	5	98	4.6	1.16	63.0	149.2	373.1	522.3	44.6	46.6	0.39
36	180	6	93	13.6	1.27	57.7	144.1	32.7	176.8	78.5	15.0	4.40
36	181	5	92	14.0	1.38	54.5	160.0	39.7	199.7	103.1	16.6	4.03
36	182	5	107	15.2	1.72	53.0	116.6	68.5	185.1	68.5	18.0	1.70
36	183	5	86	5.8	0.87	64.7	84.9	235.0	319.9	42.5	26.6	0.36
36	184	6	89	4.0	1.19	60.0	41.2	310.3	351.5	20.6	28.3	0.13
36	185	6	81	6.0	1.13	63.7	52.5	375.6	428.1	22.4	31.6	0.14
36	186	6	88	5.6	1.00	61.0	34.8	382.6	417.4	41.7	33.3	0.09
36	187	5	99	12.2	1.00	57.4	89.1	222.7	311.8	59.4	28.0	0.40
36	188	6	88	14.8	1.38	50.7	76.3	97.2	173.5	104.3	13.9	0.78
36	189	5	101	15.8	1.47	53.1	72.5	145.0	217.5	79.6	20.0	0.50
36	190	6	99	5.6	1.23	58.4	80.1	277.1	357.2	43.1	32.2	0.28

in these experiments the yield of oil rose to 47-58 ml/m^3. Thus n-butene, like ethylene and propene, does not undergo the hydrocondensation reaction in absence of carbon monoxide. It will be seen from the results of Experiment 176 (Table 4) that already in presence of 2.5% of carbon monoxide in the butene-hydrogen mixture this reaction is promoted: the yield of oil attains 198.2 ml/m^3. the ratio of heavy to light oil being 1.32.

In Tables 5, 6, and 7 results are given of experiments on the hydrocondensation of n-butene over one given catalyst, 36, in presence of alternately low (4-6%) and high (14-15%) concentrations of carbon monoxide. As will be seen from Table 5, the yield of oil, on going from low to high concentrations, falls sharply, while the ratio of heavy to light oil increases greatly. Thus the yield of oil is 46.6 and 15 ml/liter hour in Experiments 179 and 180 respectively, 26.6 and 18.0 in Experiments 183 and 182, and 32.2 and 20.0 in Experiments 190 and 189. In the same experiments the volume ratios of heavy and light oils are 0.39 and 4.40; 0.36 and 1.70; 0.28 and 0:50. From Table 5 it will be seen that the activity and condensing propensity of the catalyst fall as its participation in the process increases. This follows also from the results in Table 7 when the part taken by butene in the reaction is compared for a given range of carbon monoxide concentrations. Thus in Experiments 177-178 the fraction of butene reacting is 90-94%, in Experiments 183-186 it is 76-80%, and in Experiment 90 it is 64%. However, on going from low carbon monoxide concentrations to high this fraction is considerably less: in Experiments 180-182 it is 42-54%, and in Experiments 188-189 it is 35.5-42.4%. An intermediate position is occupied by Experiment 187, in which the initial gas mixture contained 12.2% of carbon monoxide, i.e. was characterized by an intermediate carbon monoxide concentration. In this experiment the yield of oil was 28.0 ml/liter hour and the fraction of butene reacting was 55%. Regions of differing carbon monoxide concentrations differ in the ratios of reacting components H_2/CO and C_4H_8/CO. In the low-concentration range these ratios have values from 6 to 9, and in the high-concentration range their values vary around 2.

TABLE 6

Expt. No.	Composition of original gas (vol.%)[1]			Composition of effluent gas (vol.%)[2]		
	C_4H_8	H_2	CO	C_4H_8	H_2	CO
177	38.4	44.7	5.8	5.8	18.9	0.0
178	41.3	42.2	5.5	12.4	7.2	0.0
180	45.8	36.2	13.6	49.2	9.2	2.4
181	44.5	32.1	14.0	54.0	16.4	5.6
182	48.2	28.3	15.2	59.2	8.8	7.2
183	40.0	46.0	5.8	22.8	5.6	1.6
184	48.0	40.3	4.0	26.5	6.9	0.0
185	46.0	40.6	6.0	28.4	6.4	0.0
186	44.0	43.8	5.6	26.4	10.0	0.0
187	40.6	40.0	12.2	43.2	15.0	0.0
188	45.4	33.0	14.8	59.2	12.0	6.4
189	46.4	31.7	15.8	58.0	12.2	9.2
190	48.6	39.4	5.6	41.6	8.0	0.4

1) As a rule, there was about 1 liter of N_2 in the original and effluent gases.
2) The effluent gas contained 1-2% CO_2

TABLE 7

Expt. No.	CO in initial mixture (%)	Amount that reacted (%)			Amount formed (%)		Ratio of reacting volumes of:	
		C_4H_8	H_2	CO	C_4H_{10} from the reacting hydrogen	C_4H_{10} from the reacting C_4H_8	H_2 and CO (H_2/CO)	C_4H_8 and CO (C_4H_8/CO)
177	5.8	94.1	83.7	100	38.8	40.2	6.82	6.59
178	5.5	90.2	94.4	100	46.2	49.4	7.27	6.80
180	13.6	54.7	89.3	92.5	23.9	30.8	2.57	2.00
181	14.0	44.6	76.8	81.9	18.5	23.0	2.15	1.73
182	15.2	42.1	85.7	77.8	12.4	14.7	2.04	1.73
183	5.8	79.8	95.8	88.1	32.1	44.3	8.43	6.10
184	4.0	78.2	93.2	100	45.3	45.5	9.40	9.39
185	6.0	77.5	93.3	100	39.9	42.8	6.35	5.92
186	5.6	76.4	91.0	100	33.5	39.7	7.16	6.04
187	12.2	54.9	84.1	100	22.7	34.2	2.76	1.83
188	14.8	35.5	82.1	78.7	12.9	21.5	2.32	1.38
189	15.8	42.4	75.5	73.3	10.6	13.0	2.07	1.69
190	5.6	64.1	72.6	96.8	28.8	33.3	6.65	5.75

Thus, the behavior found in propene is observed also for the case of n-butene. The concentration of carbon monoxide has a powerful influence on the hydrocondensation reaction of the olefin, and at a carbon monoxide concentration of 15% this process is suppressed to a considerable extent. The causes for this behavior probably lie, as in the case of propene, in difficulties of an adsorption and steric nature. This question is of great interest and requires further investigation.

SUMMARY

1. An investigation has been made into the effect of the concentration of carbon monoxide on its hydrocondensation with propene and with n-butene.

2. It has been established that, in absence of carbon monoxide, hydrocondensation does not occur in propene - hydrogen and butene - hydrogen mixtures.

3. The highest rate for the reaction of the hydrocondensation of propene or butene with carbon monoxide occurs when 6-8% of the latter is present in the original gas mixture.

4. When the carbon monoxide concentration in the original mixture is 15-20%, the process of hydrocondensation with propene or butene is greatly retarded; this stands in contrast to the course of the process of hydrocondensation with ethylene.

Institute of Organic Chemistry
of the USSR Academy of Sciences

Received May 20, 1951

LITERATURE CITED

[1] Ya.T.Eydus, N.D.Zelinsky, N.I.Ershov, and M.I.Batuev, Bull. Acad. Sci. USSR, 6, 731 (1951).

[2] N.D.Zelinsky, Ya. T. Eidus, K.V.Puzitsky, and M.I.Batuev, Bull. Acad. Sci. USSR, 6, 647 (1950).

[3] Ya. T. Eidus, N.D.Zelinsky, N.I.Ershov, and M.I.Batuev, Bull. Acad. Sci. USSR, 4, 377 (1950); Ya.T.Eidus, N.D.Zelinsky, and N.I.Ershov, Proc. Acad. Sci., USSR, 60, 4, 599 (1948).

[4] Ya.T.Eidus, N.D.Zelinsky, and K.V.Puzitsky, Bull. Acad. Sci. USSR, 1, 110 (1949); Ya.T.Eidus and K.V.Puzitsky, Proc. Acad. Sci. USSR, 54, 1, 35 (1946).

[5] Ya.T.Eidus, N.D.Zelinsky, and K.V.Puzitsky, Bull. Acad. Sci. USSR, 3, 326 (1949).

BLANK
PAGE

THE SPLITTING-OFF OF THE ELEMENTS OF HYDROGEN HALIDE FROM MONOHALO DERIVATIVES OF HYDROCARBONS OF THE SERIES C_nH_{2n+2}

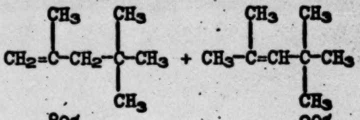
A. P. Meshcheryakov and L. V. Petrova

Markovnikov's rule [1] for the order of the addition of the elements of hydrogen halide to hydrocarbons of the series C_nH_{2n}, according to which "the halogen adds to the most hydrogenated carbon, i.e. to that which is the most subject to the influence of other carbon atoms", is confirmed by numerous facts and is generally accepted. Indications in the literature [2] of a partial change in the order of addition of HBr to isobutylene, trimethylethylene, and isopropylethylene, contrary to Markovnikov's rule, is to be explained by the presence of traces of peroxides, which cause this sort of anomaly. According to Delacr's results [3], 3,3-dimethyl-1-butene, on adding HBr, gives the primary instead of the expected secondary bromide, and this also was explained by the action of traces of peroxides. Whitmore and Homeyer [4] showed that HBr adds on to 4,4-dimethyl-1-pentene in a manner contrary to Markovnikov's rule - if we assume that in this case peroxides are absent.

Markovnikov [8] established that when hydrogen halide splits off from an alkyl monohalide the hydrogen that splits off comes not from the carbon atom to which the halogen is attached, but from the adjacent one. This rule also is confirmed by numerous facts, not only in the case of monohalides, but also, as Eltekov [5] has shown, in the case of polyhalo compounds.

Markovnikov's conclusion, that "when the elements of hydrogen halide separate from the halo compound, they always come from adjacent carbons, and the least hydrogenated carbon, even if this is connected further to highly hydrogenated carbons, has the last tendency to lose hydrogen", has been found to be erroneous in the last part of the statement. The reason for this was the inadequacy of the experimental data obtained by Markovnikov in his study of the splitting of HI from 2-iodo-3-methylbutane by the action of alcoholic caustic potash. As is well known, Zaytsev [6], on the basis of numerous facts, came to the opposite conclusion - "when a carbon that is linked to iodine is linked also to carbons having different degrees of hydrogenation, the least hydrogenated carbon has the greatest tendency to lose its hydrogen." Vagner [7], who examined the splitting of HI from 2-iodobutane, 2-iodo-2-methylbutane, and secondary hexyl iodide under the action of alcoholic potash, showed that Zaytsev's rule expresses only the predominating direction of the reaction. In those cases where Vagner showed that HI is split off in two ways, the carbon atom linked with iodine is adjacent to methyl and methylene. But if the iodine is attached to a carbon that is linked on the one hand to methyl and on the other to CH, then, according to Favorsky [8], "it is very probable that in the last case the hydrogen of the hydrogen iodide will come exclusively from the CH group." But it should be noted that also these addenda to Zaytsev's rule are based on facts obtained from a study of the halogen derivatives of hydrocarbons that do not contain quaternary carbon atoms.

As is well known, diisobutylene, which was first prepared by Butlerov [9], is a mixture of 80% 2,4,4-trimethyl-4-pentene (α-form) and 20% 2,4,4-trimethyl-3-pentene (β-form):



$$CH_2{=}C(CH_3){-}CH_2{-}C(CH_3)_2{-}CH_3 + CH_3{-}C(CH_3){=}CH{-}C(CH_3)_2{-}CH_3$$

80% (α-form) 20% (β-form)

Butlerov [9], by oxidizing diisobutylene with a 5% solution of $KMnO_4$, obtained oxoctenol (epoxyalcohol) (prismatic needles, m.p. 49.5°) and trimethylacetic acid, which are formed only from the β-form of diisobutylene.

On the basis of the amounts of oxoctenol and trimethylacetic acid obtained in the oxidation of diisobutylene by the method of Vagner [7] and Prilezhaev [10], we have derived the quantity of β-form in diisobutylene obtained by different methods. On splitting HCl (I) from 2-Cl(Br,I)-2,4,4-trimethylpentane, then according to Zaytsev we should obtain mainly the β-form of diisobutylene.

By treating 2-Cl(I)-2,4,4-trimethylpentane with alcoholic potash, we obtained as our main product, as the experiments described below will show, the β-form of diisobutylene, i.e. the elements of hydrogen halide are split off from this particular halogen compound in a manner contrary to Zaytsev's rule: the splitting-off of an H atom proceeds mainly at the most hydrogenated carbon atom, i.e. the methyl, and not the methylene. This fact is interesting as an example of a definite change in the order of splitting-off of the elements of hydrogen halide, depending on a change in the chemical structure of the organic halide molecule and therefore on a change in the nature of the mutual effects of the atoms making up the molecule. Is this property of 2-Cl(I)-2,4,4-trimethylpentane – the splitting-off of HCl(I) in a manner contrary to Zaytsev's rule – determined merely by the presence of the quaternary carbon atom, or by the neopentyl group?

According to Markovnikov [1], there is a resemblance between dehydration and the splitting off of hydrogen halide from these compounds. "All that has been said of the splitting off of water is completely applicable also to the splitting off of hydrogen halide." This is indeed confirmed by the facts: as Whitmore [11] has shown, on dehydrating dimethylneopentylcarbinol over an acid catalyst, there is formed a mixture of diisobutylenes containing 80% of the α-form and 20% of the β-form. Comparing these results for the dehydration of dimethylneopentylcarbinol with ours – by the action on 2-Cl(I)-2,4,4-trimethylpentane of alcoholic potash, the β-form of diisobutylene is formed in small quantity – very small in the case of the iodo compound.

According to Whitmore's results, dehydration of 2,2,3-trimethyl-3-pentanol gives 80% of the normal dehydration product, i.e. 2,2,3-trimethyl-3-pentene. According to our results, approximately the same amount of this olefin is obtained by the splitting off of hydrogen halide from the hydriodic ester of this same alcohol, from which it follows that when the halogen is adjacent to a methyl group and to a quaternary carbon atom (tertiary butyl), the elements of hydrogen halide are split off according to the Zaytsev-Vagner rule. However, in 2-Cl(I)-2,4,4-trimethylpentane, the neopentyl group behaves in a special way, causing the hydrogen of the methyl group, and not of the methylene group, to become the more reactive, which is evidenced by the formation of a preponderance of the α-form of diisobutylene on splitting off HCl from the halogen compound indicated.

For investigation we took diisobutylene prepared by the following methods:

1) from isobutyl alcohol by the action of 63% sulfuric acid [12];

2) from tert-butylsulfuric acid (which is prepared by saturating in the cold two volumes of 63% sulfuric acid with one volume of liquid isobutylene) by heating for one hour on the water-bath; yield of diisobutylene, b.p. 100-105°, 62-65%, and of triisobutylene, b.p. 176-179°, 37-38%;

3) by splitting off the elements of hydrogen halide from 2-Cl(I)-2,4,4-trimethylpentane.

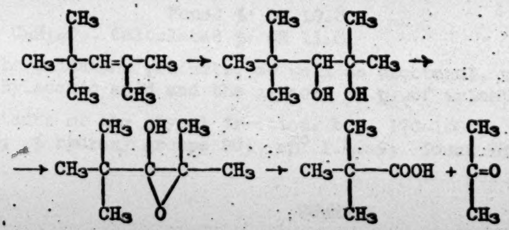
The hydrogen halide addition products were obtained by saturating the diisobutylene (cooled in ice) with gaseous HCl(HI). 2-Cl-2,4,4-trimethylpentane had b.p. 144-150°; d_4^{20} 0.8723; n_D^{20} 1.4395; calculated MR_D 44.01; found MR_D 43.70; 2-I-2,4,4-trimethylpentane had b.p. 82°/15 mm; d_4^{20} 1.2866; n_D^{20} 1.4919; calculated MR_D 51.9; found MR_D 52.4.

The properties of the original diisobutylenes are given in Table 1.

TABLE 1

No.	Original diisobutylene	B. p. (°C)	d_4^{20}	n_D^{20}	Found MR_D	Calculated MR_D
1	Diisobutylene prepared from isobutyl alcohol and 63% H_2SO_4	100-104.5	0.7211	1.4069	38.32	38.67
2	Diisobutylene prepared by splitting HCl from 2-Cl-2,4,4-trimethylpentane	100-102.5	0.7193	1.4091	38.57	38.67
3	Diisobutylene prepared by splitting HI from 2-I-2,4,4-trimethylpentane	100-105	0.7306	1.4112	38.13	38.67
4	Butlerov's diisobutylene	100-105	0.7129	1.4095	38.95	38.67

Diisobutylene was oxidized with a 1% solution of $KMnO_4$ according to Vagner [7] and Prilezhaev [10], and the amount of oxoctenol (the epoxyalcohol) and of trimethylacetic acid was determined; these, as pointed out above, are formed only in the oxidation of the β-form of diisobutylene:



The results of experiments on the oxidation of diisobutylene are given in Table 2, from which it will be seen that diisobutylene obtained from isobutyl alcohol by the action of 63% sulfuric acid contains the least amount of the β-form, since, under the action of sulfuric acid, it isomerizes into 2,3,4- and 2,2,3-trimethylpentene [12].

TABLE 2

No.	Initial product	Weight of diisobutylene taken (g)	Weight of diisobutylene unreacted (g)	Obtained (g)			Oxidized diisobutylene (g)	Yield of oxoctenol on diisobutylene taken (%)	Yield of oxoctenol on diisobutylene oxidized (%)	% β-form in the initial diisobutylene
				Oxoctenol fraction, b.p. 175-179°	Trimethylacetic acid	Glycol				
1	Diisobutylene prepared from isobutyl alcohol and 63% H_2SO_4	21	17.28	0.42	1.00	0.50	3.72	2.30	8.8	6.70
2	Diisobutylene prepared by splitting HCl from 2-Cl-2,4,4-trimethylpentane	21	17.20	1.15	1.00	1.00	3.80	4.25	23.5	10.00
3	Butlerov's diisobutylene .	36.4	10.2	4.7	3.00	3.00	26.2	10.00	14.00	19.00

On splitting off the elements of hydrogen halide from 2-Cl-2,4,4-trimethylpentane, 10% of the β-form of diisobutylene is formed, i.e. half of the amount present in the diisobutylene of Butlerov, and when HI is split off 2-I-2,4,4-trimethylpentane the amount of β-form produced is again small, for only traces of oxoctenol were found in the oxidation products, which confirms that the elements of HCl and HI are split off from these halo compounds in a manner contrary to A.M.Zaytsev's rule.

In all experiments in which diisobutylene was oxidized with 1% $KMnO_4$, oxoctenol (the apoxyalcohol) was obtained as transparent prismatic needles, m.p. 49-51°.

Analysis of oxoctenol

Found %: C 66.85; 66.63; H 11.29; 11.30.
$C_8H_{16}O_2$. Calculated %: C 66.66; H 11.11.

Determination of the number of hydroxy groups in oxoctenol according to Chugaev-Tserevitinov:

Found %: OH 10.8
$C_8H_{16}O_2$. Calculated %: OH 11.8.

In the oxidation products, as well as oxoctenol, small quantities were found of trimethylacetic acid and the glycol. B.p. of trimethylacetic acid 162-164°.

Constants of the glycol fraction: b.p. 170-180°; d_4^{20} 0.9033; calculated MR_D 40.68; % hydroxy groups 20; n_D^{20} 1.4249; found MR_D 40.78; calculated % OH - 23.

SUMMARY

1. It is shown that, on splitting off the elements of hydrogen halide by the aid of alcoholic potash from the hydrohalic esters of dimethylneopentylcarbinol [2-Cl(I)-2,4,4-trimethylpentane], the hydrogen that is necessary for the formation

of the hydrogen halide splits off from the most highly hydrogenated carbon atom - from the methyl, and not the methylene group; i.e., contrary to Zaytsev's rule.

2. This departure from Zaytsev's rule concerning the order of the splitting-off of the elements of hydrogen halide from monohalo derivatives of hydrocarbons of the C_nH_{2n+2} series is at present the only exception and is to be explained by the presence of the neopentyl radical; in just the same way the addition of hydrogen bromide to neopentylethylene in a manner contrary to Markovnikov's rule appears also to be the only exception to the rule.

3. The amount of the β-form in diisobutylene depends on the conditions of preparation. Diisobutylene prepared according to Butlerov's method contains the greatest amount of the β-form (~20%), and a considerably lower amount is obtained by splitting HCl with the aid of alcoholic alkali off 2-Cl-2,4,4-trimethylpentane (~10%) and off 2-I-2,4,4-trimethylpentane.

Institute of Organic Chemistry
of the USSR Academy of Sciences

Received May 24, 1951

LITERATURE CITED

[1] V.V.Markovnikov. Material Concerning the Mutual Influence of Atoms in Chemical Compounds. 96, Kazan, 1869.

[2] Ogonowsky. Ber., 36, 1988 (1903).

[3] Delacr. Bull.Acad.roy.Belg., 7 (1906); Chem.Soc.Abs., 90 (1), 476 (1906).

[4] Whitmore and Homeyer. J.Am.Chem.Soc., 55, 4555 (1933).

[5] A.P.Eltekov. J.Russ.Phys.Chem.Soc., 9, 386 (1877).

[6] A.M.Zaytsev. J.Russ.Phys.Chem.Soc., 7, 289 (1875).

[7] E.E.Vagner. Oxidation Reactions of Unsaturated Carbon Compounds. 47, Warsaw, 1888.

[8] A.E.Favorsky. Selected Works. Moscow-Leningrad, 1940, p. 70.

[9] A.M.Butlerov. J.Russ.Phys.Chem.Soc., 9, 41 (1877); 14, 199 (1882).

[10] N.A.Prilezhaev. J.Russ.Phys.Chem.Soc., 39, 769 (1907).

[11] F.Whitmore and Menier. J.Am.Chem.Soc., 55, 372 (1933).

[12] A.P.Meshcheryakov, M.I.Batuev, and A.D.Petrov. Bull.Acad.Sci.USSR, Div. Chem.Sci., 3, 282 (1950).

BLANK
PAGE

ISOMERIZATION OF ALKANES IN PRESENCE OF $AlCl_3$ UNDER A PRESSURE OF HYDROGEN

COMMUNICATION 1. ISOMERIZATION OF n-HEXANE

M.G.Gonikberg, A.E.Gavrilov, and B.A.Kazansky

The isomerization of n-hexane in presence of aluminum chloride was first investigated by Moldavsky and coworkers [1], who established the existence of an induction period in the isomerization and also the promoting effect of HCl. In later work by Moldavsky and Nizovkina on the isomerization of pentane [2], a hexane fraction was obtained, and investigation showed this to contain a large amount of 2,2-dimethylbutane [3]. Attention must be drawn to the work of Petrov, Meshcheryakov, and Andreev [4], and also to the investigation of Moldavsky, Kobylskaya, and Livshits [5] on the isomerization of alkanes in presence of $AlCl_3$ under a pressure of hydrogen. In this and later work [6] it was shown that it was desirable for the isomerization of alkanes in presence of $AlCl_3$ to be carried out under a pressure of hydrogen in order to suppress side reactions. However, no systematic study of the effect of the value of the pressure on the direction and rate of isomerization has yet been carried out. It has been established only that replacement of hydrogen by nitrogen results in a reversion to cracking and the formation of a "lower layer". It has been established also that isomerization occurs only in presence of moisture or HCl, even in very small quantity; in some investigations equimolecular amounts of $AlCl_3$ and HCl were used. It is very notable that when carrying out the isomerization of n-hexane under a pressure of hydrogen (of some tens of atmospheres) the catalyst remains crystalline and its active life is considerably increased. Finally, it has recently been shown [6] that addition of cycloalkanes or of small amounts of benzene to alkanes greatly suppresses cracking. The addition of powdered aluminum to the catalyst acts in the same direction. Such are the most important features of the isomerization of n-hexane in presence of $AlCl_3$ that have been known up to the present time.

In the present work we have investigated the isomerization of n-hexane in presence of hydrogen at pressures of up to 1500 atm. We used commercial aluminum chloride and n-hexane that had been purified from small amounts of contaminating unsaturated and aromatic hydrocarbons by adsorption chromatography. The physical constants of the purified n-hexane were d_4^{20} 0.6594; n_D^{20} 1.3750; data in the literature [7]: d_4^{20} 0.65937; n_D^{20} 1.37486.

The boiling point of the purified hexane was 68.4-68.8° (when the hexane was distilled through a column of 30 theoretical plates, 3% distilled between 68.1 and 68.4° at 760 mm). According to data in the literature, b.p. of n-hexane is 68.74° [7].

Parallel experiments carried out under identical conditions using hexane before and after purification showed that the presence in n-hexane of small amounts of unsaturated and aromatic hydrocarbons has no appreciable effect on the rate of isomerization, when there is no cracking.

The isomerization was carried out in a shaken reactor of 150 ml capacity made of stainless steel. n-Hexane (60 g) and the calculated amount of $AlCl_3$ (in the form of 2-4 mm pieces) were introduced into the reactor, and hydrogen was then passed in from a cylinder under a pressure of up to 140 atm. In order to carry out experiments at greater pressures, the calculated amount of $AlCl_3$ was put into the reactor, hexane was added up to half the height of the reactor, hydrogen (140 atm) was passed in, and the pressure was further increased by pumping in n-hexane by means of a pump (up to 500 atm). Still greater pressures were attained by passing hexane into the reactor from a supercharged cylinder by the aid of a compressor working at super-high pressure. This procedure was adopted in order to prevent the dissolution of large amounts of compressor lubricant in hydrogen; the solubility of the lubricant in the compressed gas rises rapidly with increase in pressure.

In our experiments at pressures of greater than 140 atm, the amount of hydrogen in the reactor was about 10 liter (on reducing to 760 mm and 0°C), which ensured the saturation of hexane with dissolved gas for pressures of up to 400-500 atm (see [8]). At pressures of the order of 1000 atm and higher, the solution of hydrogen in hexane that was formed was, of course, unsaturated. After the pressure had been established, the shaken reactor was heated by means of a cylindrical electric furnace that was fixed round it. At first the pressure fell somewhat because of the dissolution of hydrogen in the hexane, but later it began to rise. The temperature of the experiment, and the corresponding pressure, was attained in 30-35 min, and it was maintained at the desired level up to the end of the experiment; after the required time, heating was discontinued and the reactor was cooled with ice.

We first carried out experiments in which n-hexane was heated with $AlCl_3$ under the high pressure of the liquid hexane itself, in absence of hydrogen (see Table 1). In these experiments, among the reaction products were found lower- and higher-boiling hydrocarbons (relative to the hexane fraction) and a dark-colored lower layer, the presence of which indicates that an appreciable amount of cracking occurred. After being separated, the transparent upper layer was washed with dilute NaOH solution, dried ($CaCl_2$), and distilled. The lower layer was decomposed by means of ice and extracted with ether; the ether layer was washed and dried, and the solvent was distilled off.

The results in Table 1 show that the isomerization of n-hexane under pressure in absence of hydrogen is accompanied by an appreciable amount of cracking.

The succeeding experiments were carried out with n-hexane and $AlCl_3$ in presence of hydrogen, and it was found that at a sufficiently high pressure of hydrogen (and corresponding concentration of hydrogen dissolved in hexane) the formation of a lower layer was not observed. The liquid reaction products contain only a hexane fraction.[1] The external appearance of the catalyst did not alter. The clear colorless reaction product was washed and dried; it was then distilled through a fractionating column of 30 theoretical plates. This column permitted quite satisfactory separation of 2,2-dimethylbutane (b.p. 49.7°) from the other isomers: 2,3-dimethylbutane (b.p. 58.0°), 2-methylpentane (b.p. 60.3°), and 3-methylpentane (b.p. 63.3°), but it could not guarantee quantitative separation of the other isomers (Fig. 1). The total yield of isomers was judged from the amount of the total fraction of b.p. 47-66° in its relation to

---

[1] When emptying the reactor, there was generally a loss of 3-5 g of product (up to 8%) on account of its retention by aluminum chloride and of the filling of the hollow manometer spring.

TABLE 1

Isomerization of n-Hexane under Pressure in Absence of Hydrogen

No.	Wt. ratio $AlCl_3/n\text{-}C_6H_{14}$	Pressure (atm)	Temperature (°C)	Time (hr)	Yield (% of charge)		Composition of upper layer (%)			
					upper layer	lower layer	n-C_6	iso-C_6	$>C_6$	$<C_6$
1	0.35	900	72	2	90	0.3	98.0	-	-	-
2	0.50	1600	87	5	81	2.8	43.3	21.0	6.8	28.9
3	0.50	1650	100	5	46	8.6	6.4	14.3	16.8	62.5

Note: n-C_6 means n-hexane; iso-C_6 means isomers of hexane (fraction of b.p. 47-66°); $>C_6$ refers to the fraction boiling above 70°; $<C_6$ refers to the fraction boiling below 47° (by difference).

TABLE 2

Rate of Isomerization of n-Hexane at 100° under a Pressure of Hydrogen

No.	Wt. ratio $AlCl_3/n\text{-}C_6H_{14}$	Pressure (atm)	Time (hr)	Yield of liquid products (% of charge)	Yield of hexane isomers (fract. b.p. 47-66°) (% of liq. products)
1	0.1	75	6.5	95	10.0
2	0.5	80	3.0	95	21.4
3	0.5	85	7.0	89	58.4
4	0.5	95	7.0	87	54.0
5	0.5	85	10.0	94	75.3
6	1.0	90	1.5	90	11.2
7[1]	1.0	75	3.0	86	68.7
8	1.0	90	4.0	83	80.1
9	1.0	92	16.5	85	>91.0

---

1) An addition of 0.5% of benzene was made.

the amount of fractionated liquid reaction product. The results on the rate of isomerization of n-hexane under a hydrogen pressure of 75-95 atm at 100° and a wt. ratio of $AlCl_3$/n-hexane of 0.1, 0.5, and 1.0 are given in Table 2.

An examination of the results in Table 2 leads to the following conclusions:

1. Increase in the amount of catalyst greatly increases the rate of isomerization.

2. In the process of isomerization, at first a rise, and then a gradual fall in the rate of reaction is to be observed; at the very beginning of the process, the rate of isomerization is relatively low (see Expt . 6), which confirms the known fact that there is a period of induction in the reaction. The effect of pressure and temperature on the rate of isomerization of n-hexane in presence of $AlCl_3$ and hydrogen is illustrated by the results given in Table 3.

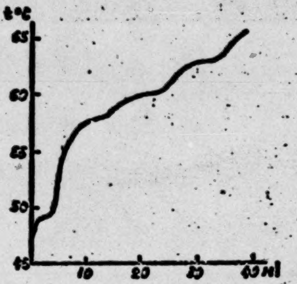


Fig. 1. Fractionation curve for hexane isomers, Expt. 7 (Table 2) at 745.7 mm (0°)

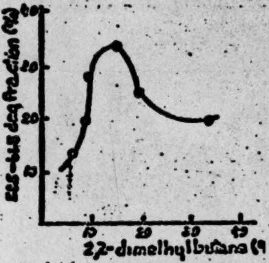


Fig. 2. Relation between the content of the 58.5-61.5° fraction and the 47-54° fraction (2,2-dimethylbutane) in the liquid reaction products (Table 5)

TABLE 3

Effect of Pressure and Temperature on the Rate of Isomerization of n-Hexane in Presence of Hydrogen

$$\left(\frac{AlCl_3}{\text{n-hexane}} = 0.5\right)$$

No.	Pressure (atm)	Temperature (°C)	Time (hr)	Yield of liquid products (% of charge)	Yield of hexane isomers (fract. b.p. 47-66°) (% of liq. products)
1	85	100	7	89	58.4
2	210	100	7	86	25.0
3	430	100	6	89	8.5
4	1450	100	13	95	5.5
5	1000	80	13	94	4.5
6	1500	125	6	91	35.6

It follows from an examination of the results given in Table 3 that increase in pressure greatly reduces the rate of isomerization of n-hexane in presence of hydrogen. Increase in temperature under these conditions greatly accelerates the isomerization (at constant pressure).

Finally, we have established that addition to the n-hexane of small quantities of benzene has a significant inhibiting effect on the cracking of n-hexane in presence of $AlCl_3$ and permits a reduction in the pressure of hydrogen necessary for carrying out the isomerization. Thus an addition of 0.5% of benzene enables the isomerization of n-hexane to be carried out without appreciable cracking at 68 atm, and an addition of 10% of benzene enables it to be carried out at 35 atm. On the other hand, the rate of isomerization of n-hexane in absence of cracking is not affected appreciably by the addition of small amounts of benzene.

The behavior observed in the isomerization of n-hexane under a pressure of hydrogen is evidence that this process, in contrast to cracking, is not inhibited by small amounts of additives that may undergo alkylation. The presence of an induction period and of a maximum isomerization rate may be explained on the hypothesis that the rate of the process is determined by at least two successive reactions [9]. Finally, the reduction in the isomerization rate that we have found for increasing hydrogen pressure makes it very probable that the isomerization of n-hexane must involve the separation of hydrogen in one of its intermediate stages[1]. If such an intermediate stage occurs in the reaction, then increase in hydrogen pressure will have a delaying effect on the isomerization process for the following reasons: In the first place, it will lead to an increase in the concentration of dissolved hydrogen and so reduce the equilibrium concentration of the intermediate product. In the second place, at sufficiently high pressures the effect of pressure also as a physical factor will begin to tell on the actual value of the equilibrium constant for this intermediate stage of the reaction, which takes place with increase in volume. It should be noted that in order to determine the mechanism of the isomerization of alkanes under a high pressure of hydrogen careful study must be devoted to the part played by cracking products, the formation of which (in small quantities) cannot be altogether excluded under these conditions.

We will turn now to an examination of the composition of the mixture of isomers obtained in the present investigation. It follows from the above results that under suitable conditions the isomerization of n-hexane may proceed to an extent of greater than 80%. It was found at the same time that the content of 2,2-dimethylbutane grows considerably in the final stage of the isomerization and that there is a simultaneous fall in the content of 2-methylpentane.

In Table 4 some results are given of the fractionation (content of fractions of b.p. 47-54° and 58.5-61.5°) of liquid reaction products for all experiments in which a degree of isomerization of greater than 50% was attained. The fraction of b.p. 47-54° consists of 2,2-dimethylbutane, sufficiently well separated from the remaining isomers; the fraction of b.p. 58.5-61.5° contains mainly 2-methylpentane.

From the results in Table 4 it will be evident that the content of the 58.5-61.5° fraction passes through a clearly defined maximum at a definite 2,2-dimethylbutane content[2] (Fig. 2).

These results lead to the conclusion that the formation of 2-methylpentane forms an intermediate stage in the isomerization of n-hexane; the isomerization of 2-methylpentane evidently leads to the formation of 2,2-dimethylbutane. The part played by the remaining isomers (2,3-dimethylbutane and 3-methylpentane) and their place in the scheme of the stepwise isomerization of n-hexane demand further detailed study. In foreign literature there have recently appeared data that confirm our conclusions concerning the stepwise isomerization of n-hexane [11].

---

[1] Results on the separation of small amounts of hydrogen in the initial stage of the isomerizaton of butane speak in favor of this supposition [10].

[2] A maximum, quite as definite, is shown also by the amount of the 56-61.5° fraction, which contains mainly 2-methylpentane and 2,3-dimethylbutane.

TABLE 4

Yield of Isomerization Products
(% on Weight o. Liquid Reaction Products)

No.	Fraction of b.p. 47-66°	Including	
		Fract. 47-54°	Fract. 58.5-61.5°
1	54.0	6.0	12.9
2	68.6	8.5	19.4
3	68.7	8.7	19.6
4	75.3	9.2	28.1
5	93.0	14.8	23.8
6	80.1	18.5	25.0
7	>91.0	31.5	19.2

SUMMARY

1. It has been confirmed that by carrying out the isomerization of n-hexane in presence of $AlCl_3$ under a high pressure of hydrogen cracking is reduced to a minimum and the formation of the so-called "lower layer" in the reaction products is completely avoided.

2. It has been established that increase in the hydrogen pressure reduces the rate of isomerization of n-hexane.

3. It has been established that the isomerization of n-hexane has a stepwise character; thus 2-methylpentane evidently forms an intermediate product in the formation of 2,2-dimethylbutane.

4. Some general suggestions have been made concerning the mechanism of the isomerization of n-hexane in presence of $AlCl_3$ under a pressure of hydrogen.

Draftsman-designer Opekunov and mechanic Kuznetsov took part in the work.

Institute of Organic Chemistry of the
U.S.S.R. Academy of Sciences

Received May 25, 1951

LITERATURE CITED

[1] B.L.Moldavsky, M.V.Kobylskaya, and S.E.Livshits, J.Gen.Chem. 5, 1791 (1935).
[2] B.L.Moldavsky and T.Nizovkina, J.Gen.Chem. 10, 1183 (1940).
[3] B.L.Moldavsky, E. Nebylova, and T.Nizovkina, J.Gen.Chem. 14, 343 (1944).
[4] A.D.Petrov, A.P.Meshcheryakov, and D.N.Andreev, J.Gen.Chem. 5, 972 (1935).
[5] B.M.Moldavsky, M.V.Kobylskaya, and S.E.Livshits, J.Gen.Chem. 6, 616 (1936).
[6] Cf. Advances in Catalysis and Related Subjects, Vol. I, 1948, 244-252.
[7] A. Forziati, A.R.Glasgow, C.B.Willingham, F.D.Rossini, J. Res. Nat. Bur. Stand., 36, 129 (1946).
[8] K. Frolich, E.J.Tauch, I.I.Hogan, A.A.Peer, Ind. Eng. Chem. 23, 548 (1931).
[9] A.V.Rakovsky, Z. phys. Chem. 57, 321 (1907).
[10] E.S.Bloch, H. Pines, L. Schmerling, J.Am.Chem.Soc., 68, 153 (1946).
[11] B.L.Evering, R.C.Waugh, Ind. Eng. Chem. 43, 1820 (1951).

KINETICS OF THE DEHYDRATION OF ALCOHOLS IN PRESENCE OF TRICALCIUM PHOSPHATE

L. Kh. Freydlin and A. M. Levit

Among the most active and specific catalysts for the dehydration of alcohols are the oxides of aluminum [1], tungsten [2], and thorium [3]. In chemical practice, aluminum oxide has received particularly wide application. Very little investigation and practically no application have been received by the readily available and easily prepared phosphate catalysts. Thus there are only some brief indications in the literature of the dehydrating action of tricalcium phosphate. Allardyce [4] investigated the dehydration of isopropyl alcohol and Schwabb that of ethyl alcohol over calcium triphosphate [5]. We have used calcium triphosphate with success as a catalyst for the dehydration of formic acid [6].

The present work is devoted to a study of the kinetics of the dehydration of a number of alcohols, viz. ethyl, n-propyl, n-butyl, isopropyl, and isobutyl, in the presence of the same catalyst. The results that we have obtained show that tricalcium phosphate is a very active and specific catalyst for the dehydration of alcohols.

In investigating the effect of molecular weight, the position of the OH group in the alcohol molecule, and the structure of the hydrocarbon radical on the kinetics of the reaction we found that the order followed by the dehydration rates of various alcohols on a phosphate catalyst is the same as that followed on aluminum oxide in the investigations of Bork and Tolstopyatova [7]. The most readily dehydrated are isopropyl and isobutyl alcohol, and then follow the normal alcohols: n-butyl, n-propyl, and ethyl alcohol. The dehydration rate of a normal alcohol is the greater, the higher its molecular weight (see Table 8 and Figure 8). We have calculated the apparent activation energy $\underline{Q}$ for the dehydration reaction of alcohols; the values obtained are: ethyl 40,600 cal/mole, n-propyl 38,600, isopropyl 37,800, n-butyl 55,000, and isobutyl 68,000 cal/mole. This shows that on replacing an α-hydrogen of ethyl alcohol by a CH_3 group the activation energy for the reaction is lowered by 2800 cal/mole. On replacing a β-hydrogen by CH_3, the activation energy is lowered by 2000 cal/mole. An analogous phenomenon was observed by Dohse [8], Adadyrov [2], and Bork [7] in the dehydration of alcohols over other catalysts. As regards the introduction of CH_3 in the γ-position, our results for the butyl alcohols show an anomaly here: in presence of a phosphate catalyst, the activation energy for the reaction is not lowered, but raised. It is possible that the side-reaction of polymerization, the products of which were, in fact, found in the catalyzates of these alcohols, has an effect here.

The values of the pre-exponential factor (K_0) for ethyl, n-propyl, and isopropyl alcohols are close together: 4×10^{15}, 5×10^{15}, and 4×10^{16}, whereas for the butyl alcohols they attain the values: 3×10^{21} and 5×10^{24}.

As we have previously pointed out [6], dehydration catalysts usually contain chemically bound water, which they retain firmly. When subjected to thermal treatment, they are almost completely deactivated. Tricalcium phosphate also contains chemically bound water, which it retains firmly even at 500-600°. When tricalcium phosphate is calcined, its activity is greatly reduced. The view that we have previously advanced [9], according to which the active centers of the catalyst are to be regarded as OH groups containing a mobile hydrogen atom, is confirmed in our experiments with calcium phosphate and silica gel. We have established that the addition to them of potassium carbonate does in fact deactivate them for the alcohol-dehydration reaction.

A comparison of the rates of dehydration of ethyl alcohol and of diethyl ether shows that diethyl ether is not an essential intermediate product for the formation of ethylene from alcohol in presence of tricalcium phosphate.

Rollet [10] recommends silica gel as a catalyst in the preparation of unsaturated hydrocarbons from the lower alcohols. We made an attempt to study the kinetics of the dehydration of alcohols over silica gel. It was found that the catalyst was rapidly poisoned, an effect evidently associated with the formation of polymer film on the surface of the catalyst. We were successful in studying the kinetics of the dehydration only in the case of ethyl alcohol in the range 352-392°. The activation energy of the reaction is 22,500 cal/mole, i.e. twice as low as on phosphate. The value of K_0 is also considerably lower, being 1.3×10^9.

EXPERIMENTAL

Experimental Conditions

The apparatus and experimental procedure have already been described [11]. The alcohol was introduced into the reaction tube at the rate of 0.16 ml/min. Tricalcium phosphate was prepared from calcium chloride and ammonium phosphate. The volume of the catalyst was 20 ml, and its weight was 9 g. In all the figures given in this paper, the relation between the degree of conversion and the temperature is shown on the left, and the conformity with the Arrhenius equation is shown on the right.

Kinetics of the Dehydration of Ethyl Alcohol

As will be seen from Table 1 and Figure 1, the degree of conversion of ethyl alcohol in presence of tricalcium phosphate rises from 3.2 to 48.4% when the temperature rises from 333 to 387°. The gas obtained contains 98-99% of ethylene. $Q = 40{,}600$ cal/mole; $K_0 = 4 \cdot 10^{15}$. The catalyst is stable; it retains its activity unchanged over the course of many hours.

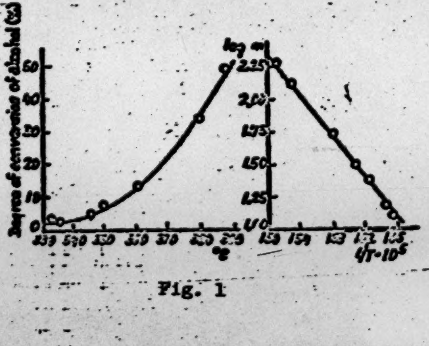


Fig. 1

Kinetics of the Dehydration of n-Propyl Alcohol

It will be seen from Table 2 and Figure 2, that when the temperature was increased from 322 to 356°, the degree of conversion of the alcohol rose from 8.2 to 46.4%. The propene content of the gas was 99%. $Q = 38{,}600$ cal/mole, $K_0 = 5 \cdot 10^{15}$. The activity of the catalyst was checked systematically over 5 hours, and no change was detected. When the tricalcium phosphate was treated with potassium carbonate (5%), the degree of the conversion of the propyl alcohol at 356° was only 3%, whereas for the catalyst that did not contain potash 47% of alcohol was dehydrated under these conditions. Hence the activity of the catalyst was reduced 15 times by the addition of potash.

TABLE 1

Kinetics of the Dehydration of Ethyl Alcohol in Presence of Calcined Tricalcium Phosphate

Ethylene content in gas 98-99%; Q = 40,600 cal/mole; $K_o = 4 \cdot 10^{15}$

Temp. of experiment (°C)	Gas liberated per 1 ml of alcohol (ml)	Degree of conversion of the alcohol (%)
333	12.2	3.2
335	13.8	3.6
345	22.0	5.7
348	30.0	7.8
360	53.0	13.8
379	132.0	34.3
387	186.0	48.4

TABLE 2

Kinetics of the Dehydration of n-Propyl Alcohol in the Presence of Calcined Tricalcium Phosphate

Propene content in gas 99%; Q = 38,600 cal/mole; $K_o = 5 \cdot 10^{15}$

Temp. of experiment (°C)	Gas liberated per 1 ml of alcohol (ml)	Degree of conversion of the alcohol (%)
322	24.5	8.2
335	47.5	15.8
347	90.6	30.2
356	139.1	46.4

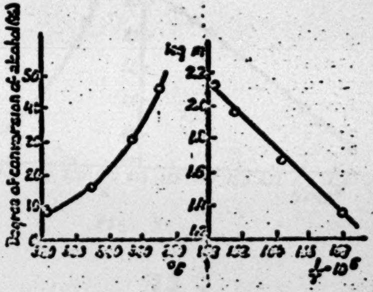


Fig. 2

Kinetics of the Dehydration of Isopropyl Alcohol

As will be seen from Table 3 and Figure 3, when the temperature was increased from 262 to 297°, the degree of conversion of the alcohol rose from 6.1 to 61.8%. The propene content of the gas was 99%. Q = 37,800 cal/mole; $K_o = 4 \cdot 10^{16}$. It will be seen from Table 3 that the dehydration of the secondary alcohol occurs at considerably lower temperatures than that of the primary alcohols. After the catalyst had been calcined at 850° for 4 hours, its activity was greatly reduced, and the yield of propene at 296° fell from 61.4% to 1.7%, i.e. to 36 times less. The activity of the catalyst with respect to the reaction of dehydration of formic acid under analogous conditions suffered only a two-fold reduction.

Kinetics of the Dehydration of n-Butyl Alcohol

It follows from Table 4 and Figure 4 that with increase in temperature from 319 to 353° dehydration of the alcohol increased from 6 to 69%. The butene content of the gas was 99%. Q = 55,000 cal/mole, $K_o = 3 \cdot 10^{21}$. Comparison of these kinetic functions with those for ethyl and propyl alcohols reveals a great increase in the values of $\underline{Q}$ and $\underline{K_o}$. It was not found possible to increase the degree of conversion of n-butyl alcohol to higher than 81% by increase in temperature.

TABLE 3

Kinetics of the Dehydration of Isopropyl Alcohol in Presence of Calcined Tricalcium Phosphate

Propene content in gas 99%; Q = 37,800 cal/mole; $K_o = 4\cdot10^{16}$.

Temp. of experiment (°C)	Gas liberated per 1 ml of alcohol (ml)	Degree of conversion of alcohol (%)
262	18.0	6.1
268	30.6	10.4
272	38.1	13.0
288	108.8	37.1
292	128.1	43.4
294	141.9	48.4
297	181.2	61.8

Kinetics of the Dehydration of Isobutyl Alcohol

It will be seen from Table 5 and Figure 5 that with increase in temperature from 312 to 334° the degree of dehydration of the alcohol rose from 12 to 80%. The content in the gas of butenes was 99%. Q = 68,000 cal/mole; $K_o = 5\cdot10^{24}$. Here, as also in the dehydration of n-butyl alcohol, a great increase in the values of Q and K_o is to be observed. It was not found possible to increase the degree of dehydration of isobutyl alcohol to higher than 80% by increase in temperature.

Effect of the Calcination of the Phosphate Catalyst on the Kinetics of the Dehydration of Ethyl Alcohol

It follows from Table 6 and Figure 6 that after calcination of the catalyst at 600-700° for 1 hour its activity is reduced about fivefold. Hence, in order to determine the kinetics, it was necessary to carry out the reaction in the higher-temperature range. In spite of the great diminution in activity, the energy of activation for the process suffered little change.

TABLE 4

Kinetics of the Dehydration of n-Butyl Alcohol in the Presence of Calcined Tricalcium Phosphate

Butene content in gas 99%; Q = 55,000 cal/mole; $K_o = 3\cdot10^{21}$.

Temp. of experiment (°C)	Gas liberated per 1 ml of alcohol (ml)	Degree of conversion of the alcohol(%)
319	14.4	6.0
332	41.6	17.2
343	99.0	40.9
351	155.2	64.1
353	168.0	69.0

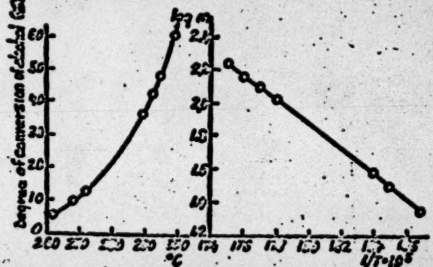


Fig. 3

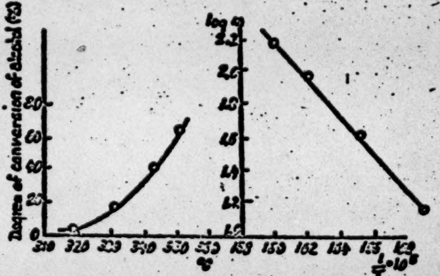


Fig. 4

Comparison of the Kinetics of the Dehydration of Ethyl Alcohol and of Diethyl Ether on Tricalcium Phosphate

When investigating the dehydration of various alcohols and their corresponding ethers on aluminum oxide over the temperature range 280-440°, Adkins and Perkins [12] concluded that dibutyl ether is not an essential intermediate product in the formation of butene because it is dehydrated considerably more slowly than butyl alcohol. The rate of dehydration of diethyl ether was found to be equal to the rate of dehydration of ethyl alcohol. On the other hand, it was shown by Bischoff and Adkins [13] that on TiO_2 ethyl alcohol is dehydrated more rapidly than ether.

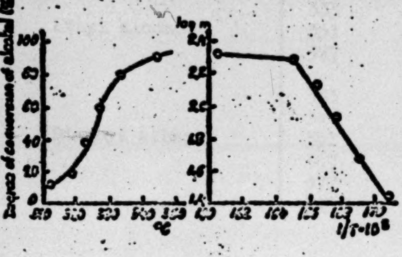


Fig. 5

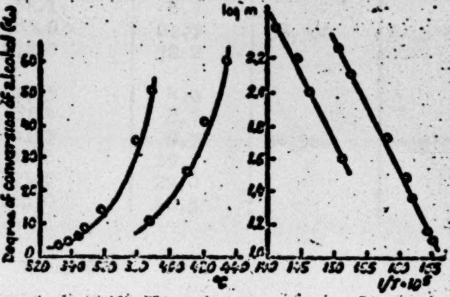


Fig. 6

TABLE 5

Kinetics of the Dehydration of Isobutyl Alcohol in the Presence of Calcined Tricalcium Phosphate

Butene content in gas 99%; Q = 68,000 cal/mole; $K_0 = 5 \cdot 10^{24}$.

Temp. of experiment (°C)	Gas liberated per 1 ml of alcohol (ml)	Degree of conversion of alcohol (%)
312	28.7	11.9
318	47.0	19.4
323	88.3	36.5
327	141.0	58.3
334	194.4	80.2

TABLE 6

Kinetics of the Dehydration of Ethyl Alcohol in Presence of Calcined Tricalcium Phosphate

Q = 36,000 cal/mole; $K_0 = 5 \cdot 10^{13}$.

Temp. of experiment (°C)	Gas liberated per 1 ml of alcohol (ml)	Degree of conversion of the alcohol(%)
388	39	10.1
410	100	26.0
420	162	42.1
434	231	60.0

In our experiments on the dehydration of ethyl alcohol on tricalcium phosphate, we found a trace of ether in the catalyzate. In order to determine whether ether is an essential intermediate product in the formation of ethylene from alcohol, we studied the kinetics of the dehydration of ethyl alcohol and of diethyl

TABLE 7

Kinetics of the Dehydration of Ethyl Alcohol and of Diethyl Ether in Presence of Calcined Tricalcium Phosphate

Substance undergoing dehydration	Temp. of experiment (°C)	Gas liberated per ml of liquid (ml)	Degree of conversion (%)	Activation energy (cal/mole)	K_0
Ethyl alcohol	326	23.0	6.0	38,300	$2 \cdot 10^{15}$
	333	32.1	8.3		
	351	83.0	21.5		
	377	278.2	72.2		
Diethyl ether	333	17.3	4.0	34,500	$5 \cdot 10^{13}$
	348	37.4	8.7		
	351	41.7	9.7		
	367	85.2	19.7		
	377	125.0	29.0		
	395	186.0	48.3		

TABLE 8

Kinetics of the Dehydration of Alcohols in Presence of Calcined Tricalcium Phosphate

Name of alcohol	Investigated temp. range (°C)	Content of unsaturated substances in gas (%)	Activation energy Q (cal/mole)	Change in the value of $Q^{1)}$ (cal/mole)	K_0	Change in $\log K_0{}^{1)}$
Ethyl	333-387	98-99	40,600	–	$4 \cdot 10^{15}$	–
n-Propyl	322-356	99	38,600	−2000	$5 \cdot 10^{15}$	–
Isopropyl	262-297	99	37,800	−2800	$4 \cdot 10^{16}$	1
n-Butyl	319-353	99	55,000	+14400	$3 \cdot 10^{21}$	6
Isobutyl	312-334	99	68,000	+27400	$5 \cdot 10^{24}$	9
Ethyl, in presence of calcined $Ca_3(PO_4)_2$	388-434	–	36,000	−4600	$5 \cdot 10^{13}$	−2
Diethyl ether in presence of calcium phosphate	333-395	–	34,500	−6100	$5 \cdot 10^{13}$	−2
Ethyl alcohol in presence of silica gel . . .	352-391	93-94	22,500	–	$1.3 \cdot 10^{9}$	–

---

1) with respect to the value found for ethyl alcohol.

ether when passed at the same molar velocity, 0.087 and 0.160 ml/min respectively, over the same sample of calcium phosphate. As will be seen from Table 7 and Figure 7, the rate of dehydration of diethyl ether was found to be about half that of ethyl alcohol.

For this new sample of phosphate the following kinetic data were obtained:

For alcohol: $Q = 38{,}300$ cal/mole; $K_0 = 2 \cdot 10^{15}$
For ether: $Q = 34{,}500$ cal/mole; $K_0 = 5 \cdot 10^{13}$.

The results obtained show that although in the dehydration of ethyl alcohol in presence of tricalcium phosphate some diethyl ether is formed, as well as ethylene, the ether is not an intermediate product in the formation of ethylene.

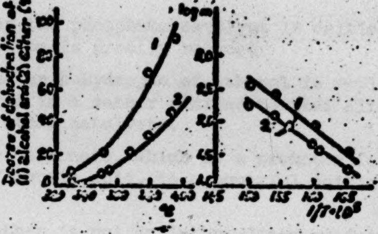


Fig. 7

Kinetics of the Dehydration of Ethyl Alcohol in Presence of Silica Gel

Comparison of the results in Table 9 and in Table 1 shows that the activity and specificity of silica gel in the dehydration of alcohols are appreciably less than those of the phosphate catalyst. With increase in temperature from 352 to 392°, the degree of conversion of ethyl alcohol rose from 4.9 to 14.9%. The ethylene content of the gas was 93%. Q = 22,500 cal/mole, $K_0 = 1.3 \cdot 10^9$. Silica gel maintains its activity for a comparatively short time, and after it has been calcined at 800° for 5 hours its activity is reduced fourfold. Thus, the calcination of silica gel has a considerably greater effect on its activity in the dehydration of alcohol than in the dehydration of formic acid.

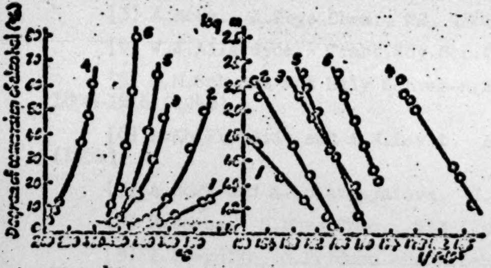


Fig. 8. Kinetic curves for the dehydration of alcohols: 1) ethyl alcohol on silica gel; 2) ethyl alcohol on phosphate; 3) n-propyl alcohol on phosphate; 4) isopropyl alcohol on phosphate; 5) n-butyl alcohol on phosphate; 6) isobutyl alcohol on phosphate.

TABLE 9

Kinetics of the Dehydration of Ethyl Alcohol in Presence of Silica Gel

Ethylene content in gas 93-94%; Q = 22,500 cal/mole; $K_0 = 1.3 \cdot 10^9$

Temp. of experiment (°C)	Gas liberated per 1 ml of alcohol (ml)	Degree of conversion of the alcohol (%)
352	19.0	4.9
368	30.0	7.8
390	52.6	13.9
392	57.4	14.9

SUMMARY

An investigation has been made into the kinetics of the dehydration in presence of tricalcium phosphate as catalyst of ethyl, n-propyl, isopropyl, n-butyl, and isobutyl alcohols.

1. It has been established that in presence of tricalcium phosphate the dehydration of alcohols proceeds in a very selective fashion, the content of unsaturated compounds in the gas being 98-99%

2. It has been found that in presence of tricalcium phosphate secondary alcohols are the most readily dehydrated, then follow the iso-alcohols, and

finally the normal alcohols. The rate of dehydration of normal alcohols falls with fall in molecular weight.

3. It has been established that when the phosphate catalyst is calcined its activity in the alcohol-dehydration reaction is greatly reduced.

4. It has been shown that when an α- or β-hydrogen of ethanol is replaced by methyl the activation energy is lowered in a manner similar to that already observed for dehydration in presence of other catalysts.

5. It has been found that potassium carbonate, which is a promoter for the phosphate catalyst in the dehydration of formic acid, is a powerful poison for it in the dehydration of alcohols.

6. It has been shown that diethyl ether is not an intermediate product in the formation of ethylene from ethyl alcohol.

Institute of Organic Chemistry
of the USSR Academy of Sciences

Received February 27, 1951

LITERATURE CITED

[1] A.Bork and A.Tolstopyatova. Acta Phys.Chim., 8, 577 (1938).

[2] I.Ya.Adadurov and P.Ya.Krayny. J.Phys.Chem., 5, 1121 (1934).

[3] A.Bork. J.Phys.Chem., 22, 1380 (1948).

[4] W.J.Allardyce. Trans.Roy.Soc.Canada, 3, 21, 315 (1927).

[5] G.M.Schwabb and Elly Schwab-Agallidis. J.Am.Chem.Soc., 71, N.5, 1806-1816 (1949).

[6] L.Kh.Freydlin and A.M.Levit. Bull.Acad.Sci.USSR Div.Chem.Sci., 5, 625 (1951).

[7] A.Bork and A.Tolstopyatova. J.Phys.Chem., 12, 245 (1938).

[8] H.Dohse. Z.Phys.Chem., 533 (1931).

[9] L.Freydlin, G.Fridman and A.Lebedeva. Bull.Acad.Sci.USSR, Div.Chem. Sci., No. 3 (1945).

[10] A.Rollet and H.Maurer-Stroh. Ber., 73 (B), 740 (1940).

[11] L.Kh.Freydlin and A.M.Levit. J.Gen.Chem., 7, 1255 (1951).$^{1)}$

[12] H.Adkins and P .Perkins. J.Am.Chem.Soc., 47, 1163 (1925).

[13] F.Bischoff and H.Adkins. J.Am.Chem.Soc., 47, 810 (1925).

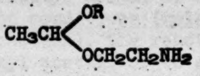
$^{1)}$ See Consultants Bureau English translation p. 1369.

THE SYNTHESIS AND REACTIONS OF VINYL ETHERS OF ETHANOLAMINES

COMMUNICATION 2. THE SYNTHESIS OF AMINOACETALS

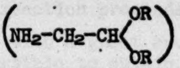
M. F. Shostakovsky, I. A. Chekulaeva, and N. A. Gershtein

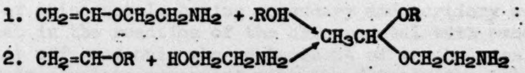
The objective of this investigation is the synthesis of aminoacetals of the following structure:



$$CH_3CH{<}\begin{matrix}OR\\OCH_2CH_2NH_2\end{matrix}$$

where R is an alkyl radical.

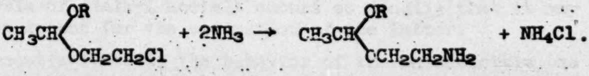
Unlike the aminoacetals that contain the amino group in the aldehyde part of the molecule  $\left(NH_2\text{-}CH_2\text{-}CH{<}\begin{matrix}OR\\OR\end{matrix}\right)$ [1,2,3,4], these compounds have received little study. In a few papers, rather complex methods for their synthesis have appeared, viz. reduction of the corresponding nitro compounds and nitriles [5,6,7]. For preparing the acetals we required, we first of all examined the simple methods developed in our laboratories of synthesizing acetals from vinyl ethers [8,9]. Two methods of synthesis were considered; they may be represented as follows:



$$\begin{matrix}1.\ CH_2{=}CH\text{-}OCH_2CH_2NH_2 + ROH\\2.\ CH_2{=}CH\text{-}OR + HOCH_2CH_2NH_2\end{matrix}\rightarrow CH_3CH{<}\begin{matrix}OR\\OCH_2CH_2NH_2\end{matrix}$$

However, it was found that the presence of the amino group in the starting substances (alcohol or vinyl ether) prevents the addition of alcohols to vinyl alkyl ethers. An attempt to remove this difficulty by replacing these vinyl ethers and alcohols containing free amino groups by their salts ($CH_2{=}CH\text{-}OCH_2CH_2NH_2\cdot HX$ and $HOCH_2CH_2NH_2\cdot HX$, where HX = HCl and CH_3COOH) also did not yield a positive result.

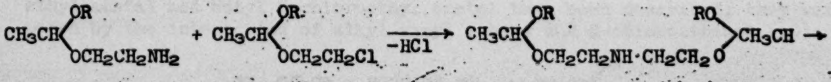
The synthesis of β-aminoethyl alkyl acetals was effected by the use of the corresponding β-chloroethyl alkyl acetals, which were caused to react with liquid ammonia:



$$CH_3CH{<}\begin{matrix}OR\\OCH_2CH_2Cl\end{matrix} + 2NH_3 \rightarrow CH_3CH{<}\begin{matrix}OR\\OCH_2CH_2NH_2\end{matrix} + NH_4Cl.$$

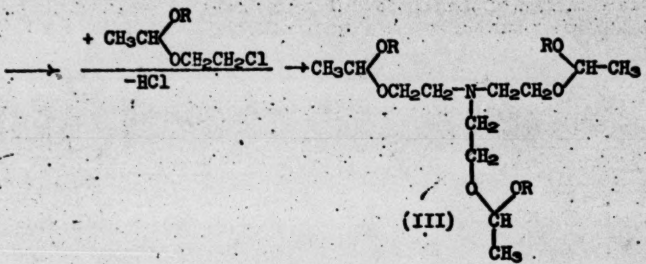
(I)

Aminoacetals containing secondary and tertiary amino groups were formed as by-products:



$$CH_3CH{<}\begin{matrix}OR\\OCH_2CH_2NH_2\end{matrix} + CH_3CH{<}\begin{matrix}OR\\OCH_2CH_2Cl\end{matrix} \xrightarrow[-HCl]{} CH_3CH{<}\begin{matrix}OR\\OCH_2CH_2NH\cdot CH_2CH_2O\end{matrix}{>}\begin{matrix}RO\\ \end{matrix}CH_3CH \rightarrow$$

(II)



(III)

This reaction was studied in some detail, the β-chloroethyl isopropyl acetal and the β-chloroethyl isobutyl acetal of acetaldehyde being taken as examples. By variation of the reaction conditions (relative amounts of the substances, temperature, duration of reaction), the reaction may be directed so as to give mainly the β-aminoethyl alkyl acetal, or to give the products of its further reaction. The results of the experiments are given in the Table, and from this it will be seen that:

1. The reaction proceeds even at room temperature, but very slowly.

2. Even with a great excess of ammonia relative to the chloroacetal (20:1), it was not possible to obtain the β-aminoethyl alkyl acetal exclusively.

3. With reduction in the excess of ammonia relative to the chloroacetal, or with increase in the duration of the reaction for a given ratio of the starting substances, the yields of the by-products, II and III, increase.

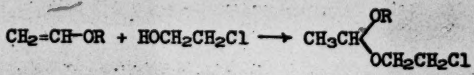
Thus, these reactions can afford one of the simplest methods for the synthesis of aminoacetals having secondary and tertiary amino groups. It was found also that in the reaction of the chloroacetal with ammonia hydrogen chloride is not split off, and only the replacement of the halogen by the amino group occurs. This is in complete agreement with the data in the literature, from which it is evident that the splitting off of hydrogen chloride from bis(β-chloroethyl) acetals and alkyl β-chloroalkyl ethers demands fairly severe conditions (reaction with alkali at 170-300°) [14].

The aminoacetals obtained have a number of peculiarities:

1. They do not undergo disproportionation under the conditions of synthesis.

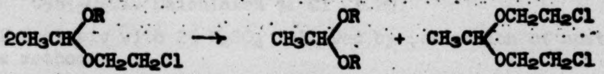
2. They are difficult to hydrolyze. Hydrolysis with 15% H_2SO_4 by heating in a closed tube on the water bath proceeds only to the extent of 80%, whereas the hydrolysis of dialkyl acetals occurs so readily that it may be used as a quantitative method for the estimation of the latter.

The peculiarities in the behavior of the aminoacetals, as also the unsuccessful attempts to prepare them from β-aminoethyl vinyl ether ($CH_2{=}CH{-}OCH_2CH_2NH_2$) and β-aminoethanol ($HOCH_2CH_2NH_2$), result from the effect of an amino group in the β-position to oxygen. The starting materials, the alkyl β-chloroethyl acetals, have also an interest of their own. In the literature, only β-chloroethyl ethyl acetal and butyl β-chloroethyl acetal have been described; they were prepared by the interaction of alkyl vinyl ethers and β-chloroethanol [10]:



$$CH_2{=}CH{-}OR + HOCH_2CH_2Cl \longrightarrow CH_3CH\begin{cases} OR \\ OCH_2CH_2Cl \end{cases}$$

We chose the same method of synthesis. At the same time we examined the effect of a radical of iso-structure on the degree of disproportionation of mixed acetals:



It was shown that also in this case there were formed, in addition to the alkyl β-chloroethyl acetal (yield 56-57% of theory), secondary reaction products: the dialkyl acetal (21-23%) and the bis(β-chloroethyl) acetal (37-44%). Hence, an iso-alkyl radical has no inhibiting effect on the disproportionation of mixed acetals.

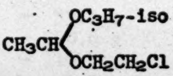
TABLE

Dependence of the Yield of Aminoacetals on Reaction Conditions

Expt. No.	Molar ratio of NH_3 to Cl-acetal	Duration of reaction, hours	Temperature of reaction, (°C)	Yield on original chloroacetal, %			
				Total yield	Of aminoacetals containing the group -NH_2	Of aminoacetals containing the group >NH	Of aminoacetals containing the group >N-
1	20:1	5-6	140-150	76.5	42.4	28.5	5.6
2	20:1	8-10	140-150	80.2	13.7	49.0	16.5
3	9:1	10	140-150	79.2	24.6	27.3	27.3
4	4:1	10	140-150	82.4	20.7	21.3	40.4
5	32:1	336	25	54.0	38.0	16.0	-

EXPERIMENTAL

I. Synthesis of β-Chloroethyl Isopropyl Acetal



$$CH_3CH\begin{cases}OC_3H_7\text{-iso}\\OCH_2CH_2Cl\end{cases}$$

The reaction was carried out in a three-necked flask with stirrer, dropping funnel, and thermometer. The starting substances were β-chloroethanol, which was purified by distilling three times, and isopropyl vinyl ether. The isopropyl vinyl ether (b.p. 54.5-55.5°; n_D^{20} 1.3850) (123.9 g) was added dropwise under stirring during 2 hours to an equimolecular amount (112.8 g) of β-chloroethanol (b.p. 126-127°; n_D^{20} 1.4407). The reaction is an exothermic one, and the temperature rose from 15 to 45°. When the vinyl ether had been added, the mixture was allowed to stand for 10-12 hours. The reaction products were fractionally distilled several times at atmospheric and at reduced pressure. The following fractions were obtained:

Fraction I, b.p. 103-122° at 760 mm - 2.5 g;
Fraction II, b.p. 123-130° at 760 mm - 30.7 g;
Fraction III, b.p. 35-72° at 22 mm - 5.2 g;
Fraction IV, b.p. 75-79° at 26 mm -138.8 g;
Fraction V, b.p. 80-100° at 26 mm - 1.0 g;
Fraction VI, b.p. 125-128° at 40 mm - 55.7 g;
239.9 g.

By vacuum distillation of Fraction IV, a product (135 g = 56.3% of theory) was isolated, which corresponded according to its analysis to β-chloroethyl isopropyl acetal: b.p. 58-61° at 10 mm;[1] n_D^{20} 1.4192; d_4^{20} 0.9865; MR_D 42.66; calculated for $C_7H_{15}O_2Cl$: MR_D 42.67; M (determined cryoscopically in benzene) 166.45; 168.2; calculated for $C_7H_{15}O_2Cl$ M 166.6.

---

[1] Most of the acetals have the property of boiling over a range of 3-5°.

Found %: C 50.56, 50.50; H 9.07, 9.32.
$C_7H_{15}O_2Cl$. Calculated %: C 50.46; H 9.07.
Found %: Cl 21.49, 21.25.
$C_7H_{15}O_2Cl$. Calculated %: Cl 21.29.

Hydrolysis with 2% H_2SO_4 followed by estimation of acetaldehyde by the bisulfite method:

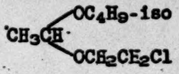
0.2059 g substance: 24.34 ml 0.1 N I_2; % acetal 98.5.
0.1936 g substance: 22.95 ml 0.1 N I_2; % acetal 98.8.

β-Chloroethyl isopropyl acetal is a colorless mobile liquid with a pleasant odor, soluble in ether, benzene, and alcohol.

Fraction II was treated with metallic sodium and distilled under atmospheric pressure. Diisopropyl acetal (25 g; 21.6% of theory) was isolated; b.p. 125-128° at 760 mm; d_4^{20} 0.8140; n_D^{20} 1.3885. Literature data: b.p. 125-128° d_4^{20} 0.8142; n_D^{20} 1.3882 [8].

Fraction VI was distilled under reduced pressure and yielded bis(β-chloroethyl) acetal (50 g; 37.0% of theory); b.p. 92-93° at 6 mm; n_D^{20} 1.4529; d_4^{20} 1.1803; MR_D 42.83; calculated for $C_6H_{12}O_2Cl_2$ MR_D 42.92. (Literature data: b.p. 104-105° at 10 mm; n_D^{20} 1.4529; d_4^{20} 1.1737 [10]; $n_D^{16.2}$ 1.4532; d_{19} 1.1712 [11].)

II. Synthesis of β-Chloroethyl Isobutyl Acetal



$$CH_3CH\begin{cases}OC_4H_9\text{-iso}\\OCH_2CH_2Cl\end{cases}$$

The experiment was carried out under conditions similar to those of the previous experiment. To β-chloroethanol (188.4 g) was added isobutyl vinyl ether (232 g)(b.p. 82-83°; n_D^{20} 1.3990) over a period of two hours. Vacuum distillation of the reaction products gave the following results.

Fraction I, b.p. 60-65° at 15 mm	- 57.4 g
Fraction II, b.p. 75-84° at 15 mm	- 240.6 g
Fraction III, b.p. 89-98° at 15 mm	- 116.8 g
Intermediate fractions	- 4.5 g
	419.3 g

After repeated vacuum fractionation of Fraction II a product (230.5 g, 56.2% of theory) was obtained as a colorless mobile liquid having the following constants: b.p. 74-77° at 11 mm; n_D^{20} 1.4230; d_4^{20} 0.9724; MR_D 47.30. Calculated for $C_8H_{17}O_2Cl$ MR_D 47.29; M (determined cryoscopically in benzene) 178.0, 178.5; calculated for $C_8H_{17}O_2Cl$: M 180.6.

Found %: C 53.06, 53.18; H 9.36, 9.49.
$C_8H_{17}O_2Cl$. Calculated %: C 53.18; H 9.49.
Found %: Cl 19.64, 19.63.
$C_8H_{17}O_2Cl$. Calculated %: Cl 19.62.

Hydrolysis with 2% H_2SO_4 followed by estimation of acetaldehyde by the bisulfite method:

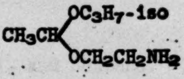
0.2775 g substance: 29.91 ml 0.1 N I_2; % acetal 97.3.
0.1786 g substance; 19.37 ml 0.1 N I_2; % acetal 97.9

The analytical results correspond to the required β-chloroethyl isobutyl acetal.

Fraction I was treated with metallic sodium and distilled, yielding diisobutyl acetal (50.1 g; 24.8% of theory); b.p. 55-57° at 8 mm; n_D^{20} 1.4025; d_4^{20} 0.8235; MR_D 51.51. Calculated for $C_{10}H_{22}O_2$ MR_D 51.66. (Literature data: b.p. 168-170°; d^{22} 0.816 [12,13].

From Fraction III, bis(β-chloroethyl) acetal was isolated (97 g, 44.5% of theory); b.p. 92-93° at 6 mm; n_D^{20} 1.4529 (see previous synthesis).

III. Synthesis of β-Aminoethyl Isopropyl Acetal



$$CH_3CH\begin{cases}OC_3H_7\text{-iso}\\OCH_2CH_2NH_2\end{cases}$$

The synthesis was carried out in a stainless steel autoclave of 150 ml capacity. The starting materials were β-chloroethyl isopropyl acetal (b.p. 58-61° at 10 mm; n_D^{20} 1.4192) and ammonia. The autoclave was cooled to −50°, and β-chloroethyl isopropyl acetal (16.4 g) and liquid ammonia (50 ml = ten times the theoretical amount) were introduced. The temperature was raised to 140-150° and was maintained at this level for 6 hours. The maximum pressure was 110 atm. The autoclave was cooled to room temperature and emptied. The gas from the autoclave was released through a valve into a flask containing water (to absorb excess ammonia) and then to a gas holder filled with salt solution. Nothing collected in the gas holder, the whole of the gas being absorbed by the water. The reaction products consisted of a dark-yellow mixture of liquid and solid. These were separated by filtering on a Buchner funnel. The residue was washed with ether. The ether was distilled off, and the residue (3.1 g) from the distillation was united with the main filtrate (9.6 g); this was distilled under reduced pressure in a stream of nitrogen. The following are the results of the fractionation:

Fraction I, b.p. 71-76° at 19 mm – 6.9 g
Fraction II, b.p. 145-155° at 6 mm – 3.8 g
Fraction III, b.p. 180-200° at 6 mm – 1.1 g
Intermediate fractions 0.9 g
12.7 g

Fraction I was repeatedly redistilled, and a substance (6.1 g: 37.2% on original chloroacetal) with the following constants was obtained: b.p. 75-76° at 20 mm; n_D^{20} 1.4240; d_4^{20} 0.9123; MR_D 41.18. Calculated for $C_7H_{17}O_2N$: MR_D 41.23; M (determined cryoscopically in benzene) 151.6, 151.5; calculated for $C_7H_{17}O_2N$ M 147.2.

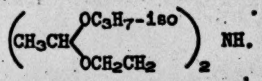
Found %: H 11.71, 11.65; C 57.0, 56.97.
$C_7H_{17}O_2N$. Calculated %: H 11.64; C 57.11.
Found %: N 9.45; 9.26.
$C_7H_{17}O_2N$. Calculated %: N 9.51.

According to these results, the product of b.p. 75-76° at 20 mm corresponds to β-aminoethyl isopropyl acetal; it is a colorless liquid with a weak ammoniacal odor, soluble in ether, benzene, alcohol, acetone, and dioxane; with a solution of sodium nitroprusside in presence of acetone it gives a violet coloration, which indicates the presence of a primary amino group.

Repeated fractionation of Fraction II in a stream of nitrogen under reduced pressure gives a second reaction product (3.0 g, 18.3% on original chloroacetal); b.p. 147-153° at 6 mm; n_D^{20} 1.4300; d_4^{20} 0.9326; MR_D 76.84; Calculated for $C_{14}H_{31}O_4N$ MRD 77.02; M (determined cryoscopically in benzene) 283.1, 281.1; calculated for $C_{14}H_{31}O_4N$: M 277.4.

Found %: C 60.47, 60.41; H 11.26, 11.37.
$C_{14}H_{31}O_4N$. Calculated %: C 60.61; H 11.26.
Found %: N 5.25, 5.12.
$C_{14}H_{31}O_4N$ Calculated %: N 5.05.

According to the analytical results, the product of b.p. 147-153° at 6 mm corresponds to the following compound:

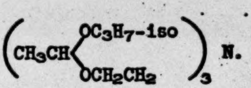


$$\left(\mathrm{CH_3CH}\begin{matrix}\mathrm{OC_3H_7\text{-}iso}\\ \mathrm{OCH_2CH_2}\end{matrix}\right)_2\mathrm{NH.}$$

It is a pale-yellow liquid, soluble in ether, alcohol, and benzene. It gives the nitroprusside color reaction that is indicative of an amino group. The solid reaction product (4.1 g) is ammonium chloride:

Found %: Cl 66.31.
NH_4Cl. Calculated %: Cl 66.36.

If the reaction conditions are altered by reducing the amount of ammonia and increasing the duration of the reaction (see Table), it is possible to increase the yield of Fraction III, from which, by vacuum distillation in a stream of nitrogen, a substance is obtained for which analysis indicates the following formula:



$$\left(\mathrm{CH_3CH}\begin{matrix}\mathrm{OC_3H_7\text{-}iso}\\ \mathrm{OCH_2CH_2}\end{matrix}\right)_3\mathrm{N.}$$

It is a yellow liquid, soluble in ether and benzene; b.p. 185-195° at 6 mm; n_D^{20} 1.4340; d_4^{20} 0.9397; MR_D 112.92; calculated for $C_{21}H_{45}O_8N$: MR_D 112.97.

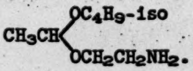
Found %: C 61.73, 61.88; H 11.17, 11.15.
$C_{21}H_{45}O_6N$. Calculated %: C 61.92; H 11.06.
Found %: N 3.86, 3.72.
$C_{21}H_{45}O_8N$. Calculated %: N 3.44.

In order to verify that the product of b.p. 185-195° at 6 mm is an individual substance, it was separated into five fractions at 2° intervals. The molecular refraction was determined for each fraction. Coincident results were obtained.

IV. The Reaction of β-Chloroethyl Isobutyl Acetal with Ammonia

The reaction was carried out in an autoclave at 140-150°, the ratio of ammonia to chloroacetal being varied (see Table). In each experiment the following aminoacetals were obtained:

1) β-Aminoethyl isobutyl acetal

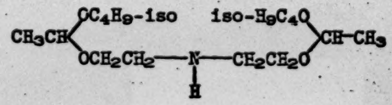


$$\mathrm{CH_3CH}\begin{matrix}\mathrm{OC_4H_9\text{-}iso}\\ \mathrm{OCH_2CH_2NH_2.}\end{matrix}$$

A colorless, mobile liquid having a weak ammoniacal odor, soluble in ether, benzene, and alcohol; b.p. 83-84° at 9 mm; n_D^{20} 1.4246; d_4^{20} 0.9000; MR_D 45.77. Calculated for $C_8H_{19}O_2N$: MR_D 45.85; M (determined cryoscopically in benzene) 158.1, 155.5; calculated for $C_8H_{19}O_2N$: M 161.2.

Found %: C 59.33, 59.17; H 11.93, 11.95.
$C_8H_{19}O_2N$. Calculated %: C 59.60; H 11.87.
Found %: N 8.36, 8.23.
$C_8H_{19}O_2N$. Calculated %: N 8.69.

2) Bis-(α-isobutoxyethyl) ether of diethanolamine



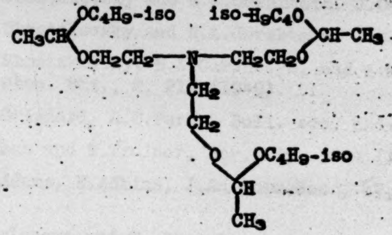
$$\mathrm{CH_3CH}\begin{matrix}\mathrm{OC_4H_9\text{-}iso}\\ \mathrm{OCH_2CH_2}\end{matrix}\!-\!\!-\!\underset{\mathrm{H}}{\underset{|}{\mathrm{N}}}\!-\!\!-\!\begin{matrix}\mathrm{iso\text{-}H_9C_4O}\\ \mathrm{CH_2CH_2O}\end{matrix}\mathrm{CH{-}CH_3}$$

A yellow liquid, soluble in ether and benzene; b.p. 160-165° at 4 mm; n_D^{20} 1.4320; d_4^{20} 0.921; MR_D 85.97; calculated for $C_{16}H_{35}O_4N$: MR_D 86.25.

M (determined cryoscopically in benzene) 304.5, 299.6; calculated for $C_{16}H_{35}O_4N$: M 305.4.

Found %: C 63.04, 62.91; H 11.55, 11.35.
$C_{16}H_{35}O_4N$. Calculated %: C 62.91; H 11.55.
Found %: N 4.76, 4.84.
$C_{16}H_{35}O_4N$. Calculated %: N 4.58.

3) Tris(α-isobutylethyl) ether of triethanolamine



A yellow liquid, soluble in ether and benzene. B.p. 210-220° at 4 mm; n_D^{20} 1.4380; d_4^{20} 0.9322; MR_D 126.6; calculated for $C_{24}H_{51}O_6N$: MR_D 126.8.

Found %: C 63.81, 63.72; H 11.40, 11.41.
$C_{24}H_{51}O_6N$. Calculated %: C 64.10; H 11.43.
Found %: N 3.43, 3.45.
$C_{24}H_{51}O_6N$. Calculated %: N 3.11.

The individuality of the product was proved by separating it into narrower fractions and determining the molecular refraction on each of these.

SUMMARY

1. β-Chloroethyl isopropyl acetal and β-chloroethyl isobutyl acetal have been prepared.

2. It has been shown that a radical of iso-structure does not inhibit the disproportionation of mixed chloroacetals.

3. β-Aminoethyl isopropyl acetal and β-aminoethyl isobutyl acetal and also aminoacetals containing secondary and tertiary amino groups have been synthesized.

4. It has been established that the yields of aminoacetals containing primary, secondary, and tertiary amino groups depend on the reaction conditions.

5. It has been found that, unlike dialkyl acetals, aminoacetals are difficult to hydrolyze and do not undergo disproportionation under the conditions of synthesis.

6. The peculiar properties of aminoacetals are to be explained by the presence in their molecules of an amino group in the β-position to oxygen.

Institute of Organic Chemistry of the
U.S.S.R. Academy of Sciences

Received June 2, 1951.

LITERATURE CITED

[1] C. Paal, L. van Geonber, Arch. Pharm. 246, 306 (1908); C.A. 3, 640 (1909).

[2] I.P.Fourneau, S. Chantalon, Bull. soc. chim. 12(5), 845 (1945).

[3] A. Wohl, Ber., 38 (4), 4154 (1905).

[4] W.O.Kermack, W.H.Perkin, P. Robinson, J.Chem.Soc., 121, 1872 (1922).

[5] M.Senkus, U.S.Patent 2,363,464 (1944); C.A. 39, 3008 (1945).

[6] D.J.Loder, U.S.Patent 2,395,281 (1946); C.A. 40, 3128 (1946).

[7] Wm. F. Cresham, U.S.Patent 2,409,675 (1946); C.A. 41, 985 (1947).

[8] M.F.Shostakovsky and N.A.Gershtein. J.Gen.Chem.16, 937 (1946).

[9] M.F.Shostakovsky and N.A.Gershtein. J.Gen.Chem. 18, 451 (1948).

[10] M.F.Shostakovsky, N.A.Gershteyn, and A.K.Gorban, Bull. Acad. Sci. U.S.S.R, Div. Chem. Sci., 2, 212 (1949).

[11] M.V.Grignard, A.C.Purdy, Bull. soc. chim. 31(4), 982 (1922).

[12] A.Claus and E.Trainer, Ber., 19, 3004 (1886).

[13] E.W.Adams, H.Adkins, J.Am.Chem.Soc., 47, 1358 (1925); J.de Girard, J. 695 (1880).

[14] A. Gulyaeva and T. Dauguleva. Caoutchouc and Rubber, 10, No. 1, 49 (1937); D.D.Coffman, U.S.Patent 2,374,078 (1945); C.A. 39, 3976 (1945).

MACROMOLECULAR COMPOUNDS

COMMUNICATION 43. SIGNIFICANCE OF ACIDOLYSIS IN THE POLYESTERIFICATION REACTION

V. V. Korshak and S. V. Vinogradova

In one of our previous communications [1] we investigated the kinetics of the acidolysis of ethyl stearate by acetic acid and showed that this ester reacts readily with acetic acid; at 250°, equilibrium is established at 44% conversion. It was interesting to elucidate the role of acidolysis in the case of dicarboxylic acids, since these are the initial materials for the preparation of polyesters. The ability of polyesters to undergo acidolysis with dicarboxylic acids was established long ago [2]. However, from the point of view of kinetics, this process has not been investigated. In order to study the acidolysis reaction, we investigated the kinetics of a model reaction, viz. ethyl stearate with succinic acid and also ethyl stearate with adipic acid.

Menshutkin [3] has shown that the process of esterifying polybasic acids is quite similar to that of esterifying monobasic acids, and the change in reaction rate in accordance with structure goes in the same direction as for monobasic acids: primary acids give the highest rate, tertiary - the lowest. According to the data available in the literature on the alcoholysis [4] and transesterification of monobasic acids [5], it may be concluded that also in the case of the transesterification of dicarboxylic acids, these laws still hold. There are few data in the literature on the reaction of acidolysis by dicarboxylic acids [6], and the kinetics of this process have, in general, not been investigated; hence, such an investigation has also a special interest of its own. The present work has for its objective the investigation of the course of the acidolysis by dicarboxylic acids with time at various temperatures, the elucidation of the effect of the ratio of the initial components on the result of transesterification, and also the determination of the effect that sulfuric acid has on the acidolysis reaction, for in the literature there are indications that sulfuric acid catalyzes the acidolysis process considerably less effectively than it does the processes of alcoholysis or simple esterification [7].

Initial Materials

The ethyl stearate employed was prepared by us by heating ethyl alcohol and stearic acid in presence of sulfuric acid as catalyst. The ester had m.p. 33° (literature data 33.7° [8]) and ester value 182 (calculated 179.5). The succinic and adipic acids were recrystallized from water and had acid values agreeing with those calculated.

Experimental Procedure

In the experiments on acidolysis by dicarboxylic acids, the procedure already applied in the investigation of the acidolysis of ethyl stearate by acetic acid [1] was employed.

Analytical Procedure

The procedure used for the analysis of the products of the acidolysis of ethyl stearate by succinic and adipic acids, in accordance with the equation

$$2C_{17}H_{35}COOC_2H_5 + HOOC(CH_2)_n \cdot COOH \rightleftarrows 2C_{17}H_{35}COOH + C_2H_5 \cdot OOC(CH_2)_nCOOC_2H_5$$

was based on the fact that the stearic acid that is formed during the reaction is insoluble in water, and it is therefore possible to make a quantitative determination of succinic or adipic acid, which is soluble in water. Thus, at 20°, the solubilities in water are: succinic acid, 5.8%; adipic acid, 1.6%, [9]. The solubilities in water of these acids may be increased by increasing the temperature.

The analysis was carried out as follows: the contents of the tube were dissolved in 100 ml of distilled water at 50-60°. After allowing to stand for 10-15 minutes with occasional shaking, the contents of the flask were cooled to room temperature. The precipitate was filtered off, and the filtrate was titrated with 0.1 N NaOH in presence of phenolphthalein. In order to verify the accuracy of the method, mixtures of equivalent amounts were taken: 1) 1 mole of adipic acid to 2 moles of ethyl stearate; 2) 1 mole of succinic acid to 2 moles of ethyl stearate. Each mixture was melted up, dissolved in distilled water, warmed to 50°, and filtered off from the residue. The filtrate was titrated with 0.1 N NaOH. Experiment showed that adipic and succinic acids titrate quantitatively in presence of phenolphthalein.

EXPERIMENTAL

a) Acidolysis of Ethyl Stearate with Succinic Acid

1. The acidolysis of ethyl stearate with succinic acid was carried out at three different temperatures: 122-123°; 168-169°; 183-184°. Ethyl stearate and succinic acid were taken in the molar ratio of 2:1. The results of the experiments are given in Table 1.

TABLE 1

Tube No.	Amount of succinic acid that has reacted, %	Duration of heating, hours	Temperature, °C
1	3.4	1	122-123
2	4.3	2	122-123
3	5.5	3	122-123
4	11.4	4	122-123
5	11.6	5	122-123
1	9.2	1	168-169
2	12.6	2	168-169
3	12.6	3	168-169
4	14.3	4	168-169
5	15.8	5	168-169
6	16.0	6	168-169
1	11.9	1	183-184
2	18.9	2	183-184
3	20.9	3	183-184
4	21.9	4	183-184

2. The effect of various ester-acid ratios on the acidolysis of ethyl stearate by succinic acid was then investigated. The tubes were heated for 5 hours at 168-169°. The results of the experiments are given in Table 2.

3. The acidolysis of ethyl stearate by succinic acid in molar ratio 2:1 in presence of sulfuric acid (1% on weight of ethyl stearate) was then investigated. The results of the experiments are given in Table 3.

b) Acidolysis of Ethyl Stearate with Adipic Acid

The acidolysis of ethyl stearate with adipic acid was carried out at four different temperatures: 122-123°; 168-169°; 183-184°; and 250°. For the

TABLE 2

Tube No.	Amount of succinic acid that has reacted, %	Molar ratio ester:acid
1	8.2	1:1
1^1	7.7	1:1
2	9.6	1:0.75
2^1	11.3	1:0.75
3	15.9	1:0.5
3^1	15.9	1:0.5
4	21.4	1:0.25
4^1	21.2	1:0.25
5	23.2	1:0.1
5^1	24.1	1:0.1

TABLE 3

Tube No.	Amount of succinic acid that has reacted, %	Duration of heating, hours
1	51.4	1
2	51.8	2
3	52.6	4
4	54.3	5

first three temperatures, the experiments were carried out by the method indicated above. For 250°, the tubes were heated in the vapor of boiling diphenyl[1]. The results of the experiments are given in Table 4.

TABLE 4

Tube No.	Amount of adipic acid that has reacted, %	Duration of heating, hours	Temperature, °C
1	7.6	1	122-123
2	11.7	3	122-123
3	13.2	4	122-123
4	13.9	5	122-123
1	13.3	1	168-169
2	18.7	3	168-169
3	19.5	4	168-169
4	22.4	5	168-169
1	14.4	1	183-184
2	16.4	2	183-184
3	19.6	3	183-184
4	23.5	4	183-184
5	23.6	5	183-184
1	16.9	1	250
2	18	2	250
3	23.4	3	250
4	27.8	4	250
5	32	5	250
6	32.4	6	250

DISCUSSION OF RESULTS

The results that we have obtained are shown graphically in Fig. 1, for the acidolysis by succinic acid (Tables 1 and 3), and in Fig. 2 for various amounts of succinic acid. On Fig. 3, the results are shown for acidolysis by adipic acid. From these figures it will be seen that both for succinic acid and for adipic acid the reaction rate increases with temperature. Thus, while the amount of succinic acid reacting at 122-123° is 11.6%, at 183-184° it attains 21.9%; for adipic acid: 13.9% at 122-123° rises to 23.6% at 183-184°, and to 32% at 250°.

Menshutkin has found that the rate of the esterification reaction falls with increase in the molecular weight of the acid. For the transesterification of ethyl stearate by adipic and succinic acids it would be expected that this rule would continue to hold, for a similar rule with respect to alcohols is maintained in the case of alcoholysis [3]. However, it will be seen from the curves that the reaction rate for adipic acid at 122-123° and 168-169° is higher than for succinic acid. This may be explained, evidently, by the fact that

---

[1] The Russian word used here is "dinyl", evidently a typographical error. CB.

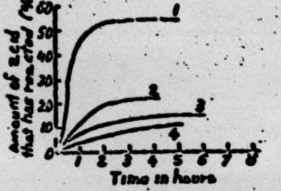


Fig. 1. 1) t 168-169°, catalyst H_2SO_4; 2) t 183-184°; 3) t 168-169°; 4) t 122-123°

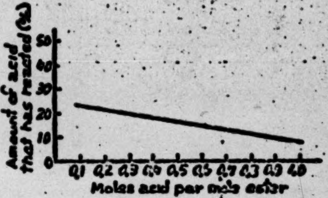


Fig. 2

succinic acid has a melting point of 183° and is in the solid state at the temperature of the reaction (succinic acid is insoluble in the ester at 183°), whereas adipic acid, which has a melting point of 153°, is soluble in the ester, and the reaction proceeds not in a heterogeneous medium, as in the case of succinic acid, but in a homogeneous one. At 183-184°, the rate of transesterification is higher in the first few hours for adipic acid than for succinic acid, but later, the rate for succinic acid becomes the higher.

TABLE 5

Temperature, °C	K	k_1 (1/g-hr.)	k_2 (1/g-hr.)	$k_1 - k_2$	m_1	m_2
250	4.32	0.222	0.956	−0.733	−0.927	0.325
183	10.4	0.111	1.15	−1.03	−0.45	0.345
168	12	0.109	1.32	−1.21	−0.387	0.314
122	38.5	0.071	2.74	−2.66	−0.194	0.165

TABLE 6

Temperature interval, °C	A_1 (cal.)	A_2 (cal.)
250-183	5540	−1490
183-168	263	−3940
168-122	3240	−5830
250-122	3870	−3490

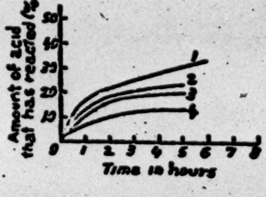


Fig. 3 1) t 250°; 2) t 183-184°; 3) t 168-169°; 4) t 122-123°

The acidolysis of the dicarboxylic acids was carried out without catalyst, and the fact that the reaction did go shows that acidolysis without catalyst is possible. It is evident that the acid itself is able in some measure to catalyze this process. In the literature there are indications [6] that sulfuric acid is not a good catalyst for acidolysis. In carrying out the acidolysis by succinic acid, an experiment was done with the objective of determining the catalytical action of sulfuric acid on the acidolysis reaction. From the curve in Fig. 1 it will be seen that sulfuric acid catalyzes the process fairly strongly.

Whereas at 168-169° without catalyst acidolysis proceeded only to the extent of 16%, in presence of sulfuric acid (1% on wt. of ethyl stearate), it proceeded to the extent of 53%, i.e. 3.3 times more rapidly. For the acidolysis of ethyl stearate by succinic acid, the effect on the reaction of the molar proportions of ester and acid was investigated (Fig. 2). It was found that with increase in the ethyl stearate:succinic acid ratio the percent acid that reacts increases.

On the basis of the results obtained (Table 4) the equilibrium constants were calculated; also the rate constants for the forward and reverse reactions (Table 5).

The data in Table 5 served for the calculation of the activation energies of the forward and reverse process, and these are given in Table 6.

The results obtained show that part (in the case of adipic acid at 250° - 32%) of the ester taken undergoes the acidolysis reaction, and in presence of catalyst as much as half of the ester reacts. From this it may be regarded as beyond doubt that also in the process of polyesterification this process of interaction between the growing molecules and the original molecule must play, together with alcoholysis, a considerable part and will determine the limiting molecular weight and molecular weight distribution in the polymers.

SUMMARY

1. The kinetics of the acidolysis reaction of ethyl stearate with succinic and adipic acids have been investigated at 122, 168, 183, and 250°.

2. It is shown that the reaction of acidolysis by dicarboxylic acids may proceed even without a catalyst; however, sulfuric acid considerably increases the reaction rate.

3. It has been found that the molar ratio of ester and dicarboxylic acid taken has an effect on the percent conversion of the acid during acidolysis. The higher this ratio, the further the reaction goes.

4. It is shown that the acidolysis reaction is of great importance in the polyesterification process.

Institute of Organic Chemistry,
U.S.S.R. Academy of Sciences

Received September 29, 1950

LITERATURE CITED

[1] V.V.Korshak and S.V.Vinogradova. Bull. Acad. Sci. USSR, Div. Chem. Sci., 2, 179 (1951).

[2] V.V.Korshak and V.V.Golubev. Bull. Acad. Sci. USSR, Div. Chem. Sci., 379 (1949).

[3] S.N.Menshutkin. J.Russ.Phys.Chem.Soc., 9, 337, 357, 377 (1877); 19, 345 (1879); 12, 82 (1880); 13, 135, 521 (1881); 14, 62 (1882); 16, 354 (1884); 17, 259 (1885); 19, 623 (1887); 23, 263 (1891).

[4] P.R.Fehlandt, H.Adkins, J.Am.Chem.Soc., 57, 193 (1935'

[5] E. Cherbuliez, M. Fuld., Arch. Sci. phys. natur. (5) 20, 143 (1937).

[6] S. Sherlock and R. Ocher, Org. Syn. 19, 45-47 (1939).

[7] E. Cherbuliez, M. Fuld, Arch. Sci. phys. natur. (5) 20, 143 (1937).

[8] L. Heintz, Ann. Phys. 87, 567 (1927).

[9] P. Karrer. Course of Organic Chemistry. Moscow, State Sci-Tech. Press, 1938, p. 370.

BLANK
PAGE

CHEMICAL CHANGES PRODUCED IN THE CELLULOSE MACROMOLECULE BY OXIDIZING AGENTS

COMMUNICATION 6. THE PRESENCE IN OXYCELLULOSES OF CARBONIC ESTER GROUPINGS AND THEIR EFFECT ON THE ESTIMATION OF URONIC CARBOXYL GROUPS

E. D. Kaverzneva, V. I. Ivanov, and A. S. Salova

In the course of our investigations into the composition of oxycelluloses, we have established that, in the determination of the uronic COOH content of oxycelluloses obtained by the action of sodium hypochlorite in acid and neutral medium, values are regularly obtained that exceed the total content of carboxyl groups in these preparations. Oxycelluloses obtained by oxidation in alkaline medium do not give this effect.

TABLE 1

Content of Total and Uronic COOH Groups in Oxycelluloses Obtained by Oxidation with NaOCl

Oxidation conditions	COOH groups equiv. to 100 gluc. res.		Difference, (1 − 2)	Oxidation conditions	COOH groups equiv. to 100 gluc. res.		Difference (1 − 2)
	By Ca acetate method (1)	Decarboxylation with 12% HCl (2)			By Ca acetate method (1)	Decarboxylation with 12% HCl (2)	
Oxidized in acid medium	0.42	0.76	−0.34	Oxidized in alkaline medium	0.38	0.43	−0.05
	0.57	1.10	−0.53		0.65	0.57	0.01
	0.74	1.04	−0.30		1.44	0.83	0.66
	2.95	3.82	−0.87		1.47	0.71	0.78
Ozidized in neutral medium	0.25	0.33	−0.08		3.49	1.58	1.91
	0.61	0.83	−0.22		4.32	3.06	1.26
	0.76	1.01	−0.95				

Similar observations were made by Kenyon and his co-workers when analyzing celluronic acids obtained by oxidation with NO_2 [1]; the cause of this phenomenon remained unknown, although these authors made a number of observations on this subject. However, behind this non-accord of two analytical methods some peculiarities in the structure of oxycelluloses that are not taken into account in the analysis may be hidden. Therefore, we considered it necessary to go into this question.

The method of determining the free COOH groups by titrating the acetic acid liberated in the reaction of the COOH groups of the oxycellulose with calcium acetate did not give us any particular reason for doubt. This method has been frequently checked and compared with other methods of determining the acidity of cellulose [2,3]. When satisfactory elimination of mineral elements from the oxycelluloses has been achieved and when correct procedure (maintenance of pH) is used, the calcium acetate method gives good agreement with the method of reversible adsorption of methylene blue and somewhat lower results in comparison with the Ag phenate method and the method of titrating with NaOH in presence of salts.

The determination of uronic COOH groups by decarboxylation with boiling 12% HCl can under certain circumstances lead to an excessive formation of CO_2. On boiling with HCl, decarboxylation occurs not only with typical uronic acids but also, with quantitative yield, with various ketocarboxylic acids. Reaction occurs also, to an insignificant extent, with many hydroxycarboxylic acids, e.g., gluconic acid, and also glyoxalic and oxalic acids [4] and compounds not containing COOH groups [5], including glucose, which yields about 0.2% CO_2 on its weight during 5 hours of reaction. However, on carrying out the reaction on pure cotton, the amount of CO_2 evolved amounts to only 0.04% by weight. Hence, the slow formation of glucose during the hydrolysis of cellulose cannot be the cause of the enhanced evolution of CO_2 during the analysis of oxycellulose.

The separation of CO_2 from non-uronic compounds is characterized by a slow rate of reaction. While, for full decarboxylation of glucuronic acid, 3-5 hours is sufficient, the formation of CO_2 from a number of carbohydrates proceeds in regular fashion, without any abatement in ten or twenty hours [4]. Hence, the presence of non-uronic compounds that yield CO_2 on boiling with 12% HCl will have an effect on the results of prolonged experiments, but will have practically no effect on the determination of uronic acids in oxycellulose under the conditions of the 5-hour boiling given in our work.

The curves for the decarboxylation of oxycelluloses in our experiments have a fairly sharp bend at 5 hours of reaction, pointing to completion of the decarboxylation of uronic acids. Slow evolution of CO_2 continues after 5 hours; it is negligible for oxycelluloses formed in alkaline medium, but is more significant for the products of acid oxidation.

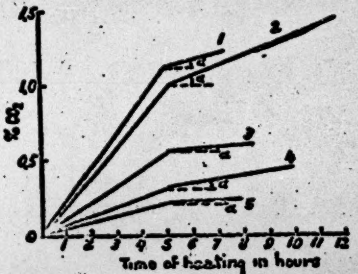
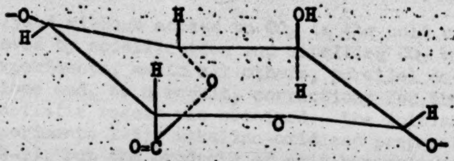


Fig. 1. Evolution of CO_2 on boiling with 12% HCl for oxycelluloses produced by acid and alkaline oxidation with hypochlorite; 1,2) pH~3; 3,5) pH 11; 4) pH 4,6.

It is clear that a very small amount of further decarboxylation is occurring. Calculation shows that these secondary reactions cannot cause an error of more than 0.02-0.04% in the estimation of uronic COOH in oxycelluloses, even if we introduce the corrections suggested by Whistler and others [5]. Apart from all these considerations, it is characteristic that an excessive amount of CO_2 is evolved only by those preparations formed by oxidation in acid or neutral medium. It is logical to suppose that this phenomenon is related to peculiarities in the structure of these oxycelluloses that have not been taken into account.

We have shown [6] that there are masked ester-linked carboxyls in oxycelluloses. We concluded that these blocked carboxyls form lactone linkages within the glucose residues and that such linkages should be formed most readily between the COOH at C-6 and the OH at C-3 in the glucose residues.



There is no doubt that such masked COOH groups will not be taken into account in methods for determining free COOH groups, but will be decarboxylated on boiling the oxycelluloses with 12% HCl and give an excessive amount of CO_2.

Thus, the most probable cause of the enhanced values, in comparison with the values for free COOH, given in the estimation of uronic COOH is the participation in the reaction of the lactonized uronic carboxyls. In order to make this conclusion quite convincing, we made a check on a number of other possible causes for the increased consumption of $Ba(OH)_2$ in the absorbers, viz.:

1) Entrainment by the passing air stream of formic acid formed during the reaction (from decomposition of carbohydrates).

2) Oxidative hydrolysis of unstable products of intermediate decomposition, with the formation of new COOH groups that undergo decarboxylation during the estimation.

3) The presence in oxycelluloses of carbonic esters that are unstable to alkalis.

As a result of our investigations, we rejected the first two of these causes and showed that it is very probable that carbonic ester groupings are present in certain oxycelluloses.

1. In experiments in which solutions of pure formic acid were boiled for 5 hours, taking amounts in excess of those that could be present when estimating uronic COOH, no appreciable carrying over of the formic acid in the air stream could be found.

The neutralization of 0.1 ml $Ba(OH)_2$, using 0.4 g of oxycellulose, gives a difference in the COOH content of 0.01%, and for a 0.2-g sample – 0.02%; these lie within the limits of the accuracy of the method.

TABLE 2

Determination of the Carry-over of Formic Acid in the Estimation of uronic COOH groups during 5 Hours of Reaction

Formic acid taken (mg)	$Ba(OH)_2$ (0.02 N) used(ml)	Formic acid carried over (mg)
1.0	0.00	0.000
2.0	0.04	0.036
2.0	0.08	0.072
30.6	0.11	0.100

2. The possibility of oxidative hydrolysis was excluded by replacing the stream of air used in the estimation of COOH groups by a stream of air-free nitrogen. This did not affect the results of the determination.

Found by analysis in stream of air (prep. No. 7) – 0.295% CO_2

Found by analysis in stream of nitrogen (prep. No. 7) $\begin{cases} - 0.290\%\ CO_2 \\ - 0.308\%\ CO_2 \end{cases}$

Consequently, oxidative processes do not cause extra evolution of CO_2 during the analysis.

3. When carbonic ester groupings are present in oxycellulose, CO_2 should split off on merely hydrolyzing with dilute alkali in the cold. In order to check on this suggestion we carried out experiments in which oxycelluloses

were hydrolyzed without access to CO_2 in the cold using CO_2-free 1% NaOH for 1 hour, followed by acidification and expelling CO_2 by blowing, also without heat. In these experiments, as in all others, parallel determinations were made on the reagents alone and, as a result, corrections for the blank were introduced. A perfectly definite result was obtained: the initial cellulose gave practically no CO_2 (Experiments 1-3), alkaline-oxidized preparations also did not react (Experiments 4-5), but the products of acid-hypochlorite oxidation gave small, but quite detectable amounts of CO_2 (Experiments 6-10).

TABLE 3

CO_2 Liberated from Oxycelluloses after Treating them with 1% NaOH in the Cold

No. of Exp.	Preparation	Amount taken (g)	CO_2 liberated (ml 0.02 N $Ba(OH)_2$	% CO_2 on amount taken	Mean % CO_2	CO_2 (equiv per 100 gluc.res.)
1	Original cellulose	1.8010	0.45	0.012	0.007	0.025
2	Original cellulose	1.2840	0.30	0.010		
3	Original cellulose	0.5160	0.00	0.00		
4	Oxycellulose, Prep.No.9	1.8560	0.05	0.010	0.005	0.018
	(alk.oxid.)	0.4610	0.05	0.001		
6	Oxycellulose, Prep. No. 7	0.5106	0.29	0.029	0.047	0.170
7	(acid oxid.)	0.4278	0.65	0.065		
8	Prep. No.1 (high degree of acid oxid.)	2.5122	2.70	0.047	0.044	0.160
9	"	2.0130	1.80	0.039		
10	"	0.5160	0.56	0.048		
11	Oxycellulose, Prep. No. 2	0.5178	0.10	0.009	0.016	0.060
12	(neut.oxid.)	1.5940	0.89	0.024		

Although the figures given in this table are very low in absolute value, they deserve to be considered, for the micro-method of determining CO_2 developed in our laboratory is distinguished by high accuracy and reproducibility, and the usual discrepancy between parallel determinations does not exceed 0.01%, as can be seen from the table.

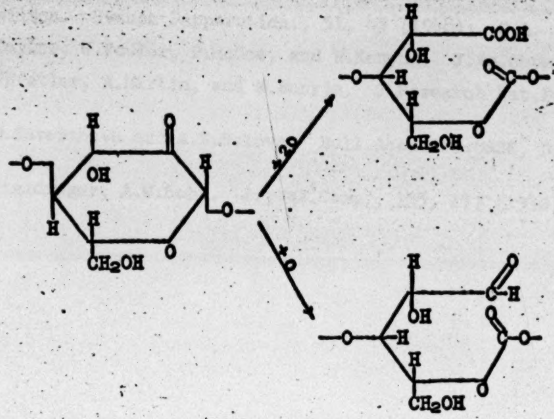
Thus, the presence in oxycelluloses formed by acid and neutral hypochlorite oxidation of a small number of linkages of the carbonic ester type is quite probable. They can be imagined to be formed by the oxidative splitting of the pyran ring at a keto group, forming a new aldehyde or carboxyl group at C-2 and a carbonate linkage at C-1. The idea of the possible presence of carbonic ester groups was expressed by Staudinger, but it was not proved in any way [7] (see p. 203).

The amounts of carbonic esters found, however, are very small and do not account for the difference between the total and uronic carboxyl contents. Oxycellulose preparations treated with alkali in the cold and therefore not containing carbonate groups gave, nevertheless, an excess amount of uronic COOH groups.

For example, Preparation No. 7 contained:

COOH groups by the Ca acetate method	0.74 equiv.per 100 gluc.res.
COOH groups (uronic)	1.04 equiv.per 100 gluc.res.
Carbonate groups	0.17 equiv.per 100 gluc.res.

COOH groups (uronic) after elimination
of carbonate groups . . . . 0.84 equiv.per 100 gluc.res.
(i.e., more than total COOH: . . . . . 0.74 equiv.per 100 gluc.res.



Hence, the presence of carbonate groups in oxycelluloses contributes to the increased liberation of CO_2 during decarboxylation, but is not the only cause. As the other sources that we have considered that could act in this direction have been eliminated, it must be admitted that the main cause of the increased content of uronic COOH groups in oxycelluloses, in comparison with the total free COOH groups, is the partial lactonization of the uronic COOH groups.

SUMMARY

1. The causes of the non-accord in determinations of total and uronic carboxyls in oxycelluloses prepared by the action of NaOCl in acid and neutral media have been elucidated.

2. It has been established that these causes are 1) the participation in reaction of lactonized carboxyls and 2) the presence in these oxycelluloses of a small proportion of carbonic ester groups.

3. The carbonic ester groups in oxycelluloses are very unstable, being readily hydrolysed by dilute alkali in the cold and by acids on warming. The presence of these groups is one of the contributing causes of the high instability towards alkalis of oxycelluloses formed by oxidation in an acid medium.

Institute of Organic Chemistry
of the USSR Academy of Sciences

Received April 21, 1951

LITERATURE CITED

[1] P. McGee, W.Fowler, and W.Kenyon. J.Am.Chem.Soc., 69, 347 (1947).

[2] G.T.Davidson. J.Text.Inst., 39 39 (1948).

[3] K.Wilson. Svensk Papperstidn., 51, 45 (1948); C.A. 42, 6535 (1948).

[4] E.Taylor, W.Fowler, P.McGee, and W.Kenyon. J.Am.Chem.Soc., 69, 342 (1947).

[5] R.Whistler, A.Martin, and M.Harris. J.Research Nat.Bur.Stand., 24, 13, (1940).

[6] E.D.Kaverzneva and A.S.Salova. Bull.Acad.Sci.USSR, Div.Chem.Sci., 6, 782 (1951).

[7] H.Staudinger, A.W.Sohn. J.prak.Chem., 155, 177 (1940).

DISCUSSION ARTICLES

ANSWER TO THE CRITICS OF THE NEW STRUCTURAL THEORY

G. V. Chelintsev

About three years ago I advanced the New Structural Theory [1], which was a development of the classical structural theory in the light of newly accumulated experimental data. An obstacle to the acceptance of the theory was the bitter opposition on the part of Ingold-Paulingites. Deprived of the possibility of defending the mesomerism-resonance theory in its direct form, they strive at least to cast the New Structural Theory from the threshold. While there is yet no new theory that can take the place of the mesomerism-resonance theory, they still retain the hope of preserving the latter in one or another disguised form.

Recently, a number of articles has been published criticizing the New Structural Theory. An examination of this criticism is bound to be useful. The general thesis of the critics of the New Structural Theory is that it is not in accord with "contemporary physics". Reutov writes [2]:"G.V.Chelintsev tries to construct his theory while ignoring the modern achievements of physics....". Kursanov, Gonikberg, Dubinin, Kabachnik, Kaverzneva, Prilezhaeva, Sokolov, and Freydlina write: "the understanding of the nature of the chemical bond demands the application and consideration of all the data yielded by modern chemistry and physics. One of the attempts at constructing a new theory of the chemical bond without taking these data into account is the "New Structural Theory" advanced by G.V.Chelintsev". One of the main propagandists of Pauling's resonance theory, Volkenshtein, writes [3]: "one cannot help expressing regret that in our day there should appear work devoted to matters of principle concerning the structure of chemical compounds which at the same time ignores the achievements of physical science. Such work (e.g., the work of G.V.Chelintsev) stands in sharp contradiction to the best traditions of the Russian vanguard of science, the traditions of A.M.Butlerov....", and so on.

The allegation that the New Structural Theory is invalid on physical grounds is based on two sorts of considerations. On the one hand, it is asserted that the law of the localization of orbitals on one or on two atoms, which is at the basis of the theory, is in direct contradiction to the quantum-mechanical concept of the wave properties of the electron and, consequently, the New Structural Theory has not taken into account the achievements of contemporary physics. This is simply a misunderstanding. Not in any quantum mechanics is there a postulate of the necessity of diffuseness in the electron on account of its wave properties - either throughout the universe of throughout the atoms of a particle. In quantum mechanics, atoms and molecules are regarded as highly organized systems, in which every electron has its own characteristics, and every orbital belongs to one or to two atomic nuclei. What is more, Pauli's principle directly defines the saturability of bonds, i.e., the inability of an electron to take part simultaneously in two covalent links, i.e., the impossibility of electron orbitals associated with three or more atoms. Thus, the law of the localization of electron orbitals on one or on two atoms is in full accord with contemporary physics, and, on the contrary, the denial of this law in the concept of the delocalization of electron orbitals is nothing more than a chemical variant of the idealistic idea of free will in an electron.

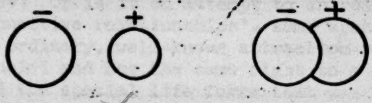
The law of the localization of electron orbitals on one or on two atoms did not originate from me; it is a direct consequence of an enormous amount of chemical experience in the expression and prediction of the various types of molecule. When put in concrete form in electronic structural formulas, the law of the localization of orbitals determines the correspondence between the number of formulas and the number of actual molecules and determines the possibilities of prediction of electronic structural theory. The law of the localization of electron orbitals in one or in two atoms molds the Butlerov teaching concerning chemical structure to the pattern of electron-nucleus concepts – only in the light of this law can the qualitative differences in the interactions of chemically linked and unlinked atoms, i.e. Butlerov's assertion of the true nature of structural formulas, be understood. If in nature the law of the localization of electron orbitals did not exist, if, indeed, the wave properties of the electron predetermined that it should have a smeared character in all atoms, then the chemical world would appear not as an assembly of discrete molecules that are mutually interconvertible in stages, but as some sort of plasma of protons and electrons.

The concept of the delocalization of electron orbitals has nothing to do with contemporary scientific physics and has been devised only in mesomerism-resonance theory. The only basis for this concept is the lack of correspondence between the formulas of conjugated compounds and experimental data. This concept is nothing more than a hypothetical assumption directed towards the elimination of this non-correspondence. Why bring in quantum mechanics, contemporary physics, etc.?

On the other hand, the allegation that the New Structural Theory is invalid on physical grounds is based also on considerations concerning the non-correspondence of the theory with experimental data obtained by modern physical methods. Here it is pointed out in particular that orbit-contact formulas for benzene, ethylene, naphthalene, anthracene, etc. are in contradiction with results that indicate the absence of a center of symmetry in the benzene molecule and the absence of a dipole moment in the ethylene, naphthalene, and anthracene molecules. As it stands, this assertion can be regarded only as the result of a gross misunderstanding. Orbit-contact formulas for benzene, ethylene, naphthalene, anthracene, etc. are possible only in the light of the concept of the homopolar electrovalent bond, and the pluses and minuses in these formulas express, as stipulated, not the polarity of the bonds, but the charges of the atoms, i.e., the excess or deficiency of electrons in the electron shells of the atoms with respect to the charges on their nuclei. The assertion concerning the non-correspondence of the orbit-contact formulas of benzene, ethylene, naphthalene, anthracene, etc. with experimental data can be considered only as a not very successful attempt to assert the absurdity of the concept of the homopolar electrovalent bond.

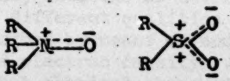
Let us see, however, whether the concept of the homopolar electrovalent bond is quite as absurd as it appears at first glance. It is generally known that dipole moments of ionic molecules are always lower in value than would be calculated for an "ideally ionic" bond. In mesomerism-resonance theory these results are applied in considerations concerning the covalent contribution in ionic bonds, and in electronic structural theory – in considerations relating to the deformations of the electronic clouds of the atoms. From all points of view the polar state of a bond is regarded not as a result of the inflexibility (non-deformability) of the electron clouds of the atoms, but as a result of the varied electrophilic characters of the atoms.

From this it follows that in the interpretation of an electrovalent bond in terms of the law of the localization of electron orbitals there can be no objection in principle against concepts concerning the possibility of leveling out the electron density in such a bond – according to the method of the deformation of electron clouds of oppositely charged atoms (shown diagrammatically):



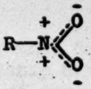
When the electrovalent atoms are of different electrophilic character, this leveling out is achieved only to a certain extent; when they have the same electrophilic character, it goes to completion, with formation of a homopolar electrovalent bond.

Acceptance of the concept of the homopolar electrovalent bond is impeded by the fact that between equally electrophilic atoms a covalent link is energetically more advantageous. However, it is possible to imagine cases in which an electrovalent arrangement in the bond is bound to occur. The notion of an electrovalent structure in a bond between atoms (generally covalently linked) that differ little in electrophilic character, such as nitrogen and oxygen, sulfur and oxygen in "semipolar systems", where the covalent arrangement is in conflict with the octet rule:



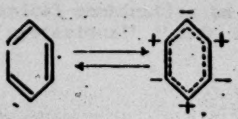
is generally accepted.

The octet rule and the fact that the lengths of the nitrogen-oxygen bonds in the nitro group are equal lead to the following formula:



from which it follows that the electrovalent bond structure may turn out to be more advantageous even in cases where a covalent bond structure is not in conflict either with the condition that there should be sharp difference in the electrophilic natures of the atoms, or with the octet rule.

It is not difficult to show that in conjugated systems, e.g., in the benzene nucleus, electrovalent bonds are preferable to covalent bonds – even when the atoms have equal electrophilic character:



It is obvious that six electrovalent bonds are energetically more advantageous than three covalent links. Hence, cyclohexatriene is pseudomeric with benzene. However, in consequence of the equal electrophilic character of the carbon atoms (and as a result of the deformation of their electron clouds), the electrovalent bonds in the benzene nucleus are homopolar. Hence, the concept of a homopolar electrovalent bond within conjugated systems is far from being an absurdity – it has both an experimental and a theoretical basis.

The critics of the New Structural Theory assert also that the concept of hypermechanical, chemically-combining interactions in molecules is tantamount to a concept of mystical "life forces". Nesmeyanov writes [4]: "Chemical bonds have a combining function! What is this, a truism after the manner of Kozma Prutkov? Or is it an attempt to introduce into science some sort of special 'connective relationships' – some special chemical force that stands outside the ordinary, well-known attraction-repulsion interactions of electrons and nuclei and has the same right to a place in science as, in the last century, did the special life force that was to explain the specificity of biological phenomena ......It is this sort of pronouncement that Chelintsev considers to be an application of dialectical materialism in chemistry!" ... "In his definition: 'reaction signifies discontinuous change in the chemical structure, preceded, accompanied, and succeeded by continuous changes in the distribution of atomic nuclei and electron density', Chelintsev again shows that he considers the quantitative changes in the distribution of nuclei and electrons only as an accompaniment, as it were, to the reaction and that he sees the causes of the appearance of a new qualitatively different state in something else – in that same mysterious chemical force that he calls a 'connective relationship'"....

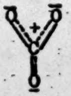
Nesmeyanov continues: " It is obvious that a chemical reaction is above all the conversion of one or several discrete particles (molecules), which possess definite qualities, into one or several other discrete particles (molecules) that possess new, different qualities and that, at the same time, this qualitative jump is performed by means of continuous changes in the distribution of atomic nuclei and electron density .... From which, of course, it does not at all follow that chemical phenomena should be reduced to physical and electrical, not to say mechanical phenomena, in just the same way as biological phenomena are not reducible to chemical and physical phenomena, although they are dependent on them and although they do not contain any supplementary life force, but constitute a qualitatively different stratum of material movement".

From all this it is clear that Nesmeyanov does not admit the possibility of any other kinds of relationship between electrons and nuclei, apart from space-force relationships, or of any other kinds of change in chemical reactions, apart from continuous rearrangement of atomic nuclei and of electron density. The phenomenon of the discrete molecule, according to Nesmeyanov, is completely embraced within the concept of an electron-nucleus aggregate, and the phenomenon of discontinuous change in the qualitative nature of molecules during reactions – within the concept of the variation of the properties of molecules. Nesmeyanov admits the irreducibility of chemical phenomena to mechanical phenomena, but considers the regarding of a chemical bond not only as "attraction-repulsion interactions of electrons and nuclei", but also as a relationship of chemical combination to be tantamount to the admission of the existence of a "mysterious" "life force".

None of this is in accord with the philosophical meanings of the concepts of discreteness, discontinuity, quality, quantity, and property. Nesmeyanov's arguments do not differ in any way from the usual arguments of mechanists who reduce the concept of quality to that of quantity, the concept of continuity to the concept of discontinuity, and the concept of the discontinuous, step-wise, qualitative change in the structure of a thing to that of a change in its properties.

The Butlerov concept of hypermechanical chemical structure is a concretization of the Engels concept of hypermechanical chemical movement. Chemical movement differs from mechanical movement in the respect that it does not consist only in the redistribution of atomic nuclei and electron density, but is accompanied by step-wise changes in the chemical-combining relationships of the electrons and nuclei of the atoms, and of the atoms themselves - changes in chemical structure. Outside the concept of chemical structure (i.e., the integrated assembly of individual chemical-combining relationships of the atoms together with the atoms themselves, and electrons and nuclei forming the molecule, which is qualitatively distinct from the general space-force relations between atoms etc., within the molecule and between molecules) the concept of hypermechanical chemical movement has no meaning. In the Butlerov concept of chemical structure we are given an attempt at learning the hypermechanical laws that apply to chemical phenomena. It is not attempts at understanding hypermechanical phenomena that lead to agnosticism and idealism, but mechanism.

Apart from the allegations considered above, the criticism of the New Structural Theory contains a number of particular remarks, which are brought together in Nesmeyanov's article "Reply to G. V. Chelintsev" [5]. Nesmeyanov considers that the occurrence of the leveling-out of bonds in the carbonate ion directly proves the truth of the concept of the delocalization of electron orbitals and that this phenomenon cannot be expressed in the formulas of the New Structural Theory. However, the New Structural Theory gives the formula of the carbonate ion as [6]:



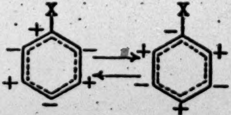
thus showing the invalidity of Nesmeyanov's allegation in both of its parts.

Also, Nesmeyanov points out that the orbit-contact formula for benzene is not in accord with the evening-out that occurs among the carbon-carbon bonds in the molecule. However, even if one ignores the concept of the homopolar electrovalent bond and erroneously interprets, as Nesmeyanov does, the pluses and minuses of the orbit-contact benzene formula (see above) not as indicating the charges on the atoms, but in the sense of bond polarity, then even in this case the intercarbon links in the formula become evened out with respect to length. In as much as Nesmeyanov gives as examples of the non-accord of the New Structural Theory with the phenomenon of the leveling-out of bonds the formulas of the carbonate ion and benzene, it is evident that the question in dispute is the leveling-out of bonds with respect to length and not with respect to the distribution of electron density between the carbons (in the carbonate ion all the bonds are polar). Nesmeyanov's assertion about the non-accord of the orbit-contact formula of benzene with the phenomenon of the leveling-cut of bonds is therefore erroneous not only in essence, but also logically.

Nesmeyanov further asserts that since the New Structural Theory makes use of the octet and tetrahedral rules it rejects the possibility of the existence of the molecules of phosphorus pentachloride, molybdenum octafluoride, etc. However, the rules of the octet and tetrahedron exist independently of the New Structural Theory, and no one has attributed to them the significance of general laws.

Nesmeyanov then rejects the New Structural Theory on the grounds that according to the theory stable aromatic molecules of cyclobutadiene and cyclo-octatetraene should be possible. However, in the New Structural Theory it was shown that [7] " aromatic rings have either five or six members because the energy required to change the valency angles in the formation of larger or smaller flat rings exceeds the gain in energy due to aromatic bond formation". Indeed, the examples of benzene, the carbonate ion, the guanidine ion, the carboxyl ion, and the nitro group show that double electrovalent-covalent (semipolar) bonds are arranged in one plane and form valency angles (for carbon or nitrogen) approximating to 120°. Thus the cited allegation of Nesmeyanov is simply a misunderstanding.

Nesmeyanov asserts also that in the New Structural Theory oscillation concepts are employed. Without these concepts it would be impossible, it is alleged, to understand how the orbit-contact formula of anthracene could be made to accord with the absence of a dipole moment in its molecule. These concepts are used directly, it is alleged, in my treatment of the absence of isomers in monosubstituted benzene:



In as much as the concept concerning oscillation is a primitive representation of the delocalization of orbitals, the New Structural Theory, being based on the law of localization of orbitals, must be regarded, according to Nesmeyanov, as inconsistent. However, the New Structural Theory has no need for oscillation concepts. The absence of a dipole moment in anthracene is to be explained by the homopolarity of its bonds, and the absence of isomeric monosubstituted benzenes — by its pseudomeric relationships [8] (in consequence of their ready interconversion, only the more stable structure exists).

Nesmeyanov points out, finally, that the orbit-contact formula of benzene is equivalent to the formulas of Vorländer and Berkenheim, which have long been rejected. It is generally known that Vorländer and Berkenheim placed pluses and minuses on the carbons of the benzene nucleus and that the phenomenon of "alternating polarity" was discovered long before the coming of the New Structural Theory. However, these formulas were rejected because they could not be defended outside the concepts of orbit and contact bonds that are given in the New Structural Theory. The criticism by Nesmeyanov of the orbit-contact formula of benzene is a proof of this — it is quite justified when applied to the formulas of Vorländer and Berkenheim, but invalid in this case. As he does not discern the difference between these formulas and does not take account of the content of the New Structural Theory, Nesmeyanov is, in fact, criticizing not this theory, but Vorländer and Berkenheim's theory. Such criticism is easy, but it misses the mark.

I must thank Nesmeyanov [9] for only two justifiable critical remarks. In the first place, I acknowledge that my application of the unverified assertion by Goldschmidt [10] concerning the presence of an axis of third-order symmetry in crystalline benzene was erroneous. In the second place, I acknowledge that my statements concerning the causes of coplanarity in conjugated and aromatic systems were erroneous also. Nevertheless, these errors, like many others which may be found, in no way affect the basic principles of the New Structural Theory.

In the same article "Reply to G. V. Chelintsev" Nesmeyanov writes: "Why does Chelintsev never make use of this 'New Structural Theory' for scientific purposes (and only for the purpose of unrestrained self-praise)........ Why on the basis of the 'New Structural Theory' has its author not made an attempt to make even a very limited prediction of new facts, not to speak of the verification of such predictions by experiment? It seems to me that there is only one answer. The author of the theory is convinced of its worthlessness — and so am I".

The question of why I do not use the New Structural Theory for scientific purposes is an obscure one. Is not my use of this theory for solving the question of the structures of hundreds of thousands of conjugated compounds, for confirming the truth of Butlerov's dialectical-materialistic teaching concerning chemical structure, for refuting the sterile Machist mesomerism-resonance theory, and for the elimination of servility and Machism from Soviet chemical science — is not my use of this theory for these purposes indeed an application of the theory for scientific purposes? As far as my conviction of the worthlessness of the New Structural Theory is concerned, is it really possible to suppose that for a number of years I could bear the whole weight of the struggle with the Ingold-Paulingites that were monopolizing Soviet chemical science, if I were not deeply convinced of the correctness and usefulness of my ideas?

There remains the question of the possibilities of prediction in the New Structural Theory. It is a great pity that this question was not put at the correct time with respect to the theory of resonance. It was several years before Nesmeyanov admitted that "The explanations given by resonance theory are illusory and, at the best, consist only of descriptions by means of an assembly of formulas" [11]. Evidently, for the determination of the possibilities of prediction in a theory, time and practice are required.

Nevertheless, let us examine what claims may be made from the New Structural Theory. It is here necessary to take into account that the New Structural Theory and mesomerism-resonance theory cannot be placed in the same category as the structure, stereochemical, co-ordination, and electron theories, with respect to their role in chemistry. Each of the latter theories reveals the laws of one or another separate variety of chemical particle (structural isomers, stereoisomers, complex compounds, radicals, and ions), and hence its formulas are suitable for the prediction of hitherto unknown particles.

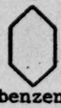
The New Structural Theory and mesomerism-resonance theory did not come into being by virtue of their application to some newly discovered separate variety of particle that did not come within the scope of previous theories. In this sense, they cannot predict anything new. However, it does not follow from this that they cannot be suitable for the prediction of a separate variety of particles. In as much as each of them is an attempt at uniting together all the theories enumerated above, it is bound to preserve all their possibilities of prediction. Consequently, the evaluation of the possibilities of prediction for the New Structural Theory and mesomerism-resonance theory with regard to a separate variety of particles can be done by suitable comparison of one theory with the other.

The superiority of the New Structural Theory is here obvious. There are preserved in it the laws and rules of the chemical combination of atoms and of atoms, electrons, and nuclei in particles which are revealed in the above-enumerated theories and embodied in their formulas — laws of the localization of orbitals and bonds, rules of valency numbers, octets, and tetrahedra, of co-ordination numbers, co-ordination, and octahedra. There are preserved in it the affirmation of the truth of these formulas and of the correspondence of each formula to one real particle, and therefore of the possibility of predicting hitherto unknown particles corresponding to formulas that have not been assigned to known particles. On the contrary, the concept of the delocalization of orbitals that lies at the basis of mesomerism-resonance theory logically leads to a rejection of the laws and rules mentioned, to affirmation of the ficticiousness of the formulas referred to, and to prediction of an unlimited number, by comparison with the number of real particles, of distributions of atomic nuclei and electron density, i.e., to complete loss of the prediction possibilities of the above-enumerated theories.

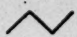
If with respect to the prediction of separate varieties of molecules the New Structural Theory preserves only the possibilities of classical theory, then with respect to the prediction of new facts in general, it will be fruitful in the highest degree. The replacement of the erroneous formulas of hundreds of thousands of conjugated compounds by correct formulas is bound to lead to the enrichment of the predicting possibilities of the theory of chemical structure. Time and practice will lead not only to confirmation of the truth of the New Structural Theory, but also to the revelation of its practical fruitfulness.

In spite of its imperfections, the New Structural Theory, even in its present form, is incomparably more practical than mesomerism-resonance theory. It will serve as a reliable basis for chemical theory at the present stage of the development of structure problem.

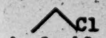
It is necessary to realize clearly that the possibility of avoiding the usual erroneous formulas for conjugated compounds provided in the formulas of Ingold and Pauling does not help, but hinders the development of chemical theory. It should be understood that no other formulas for the chemical structure of conjugated compounds apart from those of the New Structural Theory can exist on the plane of modern electron-nucleus concepts. When the significance of these formulas has been assimilated, then it will be possible to simplify them, for example:



benzene



butadiene



vinyl chloride

and they will then not only be true representations of conjugated compounds, but also practically convenient methods of representation.

Soviet chemical theory must be freed from the influences of bourgeois theory and must develop within the plane of Butlerov's dialectical-materialistic teaching concerning chemical structure.

Received February 13, 1951

LITERATURE CITED

[1] G. V. Chelintsev. Notes on the Theory of Organic Chemistry. State Chemical Press, 1949.

[2] O. A. Reutov. Problems of Philosophy, 3, 315 (1949); N. D. Kursanov, M. G. Gonikberg, B. M. Dubinin, M. I. Kabachnik, E. D. Kaverzneva, E. N. Prilezhaeva, N. D. Sokolov, and R. Kh. Freydlina. Prog. Chem., 19, 538 (1950).

[3] M. V. Volkenshtein. Prog. Chem., 19, 604 (1950).

[4] A. N. Nesmeyanov. Bull. Acad. Sci. U.S.S.R, Div. Chem. Sci., 5, 546, 549, 548 (1950).

[5] A. N. Nesmeyanov. Ibid., 541-550 (1950).

[6] G. V. Chelintsev. Notes on the Theory of Organic Chemistry. State Chemical Press, 1949, p. 99.

[7] G. V. Chelintsev. Ibid., p. 114.

[8] G. V. Chelintsev. Ibid., p. 108.

[9] A. N. Nesmeyanov. Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci., 5, 542, 544 (1950).

[10] Goldschmidt. Stereochemistry, 81 (1940).

[11] A. N. Nesmeyanov. Scientific Memoirs of the Moscow State Univ., No. 12, p. 10 (1950).

BLANK
PAGE

"CONTACT BONDS" AND THE "NEW STRUCTURAL THEORY"

A. N. Nesmeyanov

In his reply to critics of the New Structural Theory [1], Chelintsev is concerned with certain of my critical pronouncements [2]. He admitted only two of the concrete critical inferences that I made, and these directly concerned the nature and formation of "contact bonds". These were: the error made by Chelintsev in attributing an incorrect axis or third-order symmetry to crystals of benzene in his considerations concerning the structure of the benzene molecule, and his error in making the assertion that the coplanarity of olefin, aromatic, and similar molecules can be derived from the properties of the contact bond, as being a bond of octahedral origin. However, he considers that these mixtakes are special cases, admits that his New Structural Theory still contains many similar mistakes, and is convinced that these errors do not affect the basic principles of his theory. Certain other of my concrete criticisms, all concerning the same contact bond, he passes over in silence (e.g., the tetrahedral character of HgI_4'', which corresponds, according to Chelintsev's theory, to an orbit structure like that of CH_4 and therefore dissociates tetrahedrally built complex compounds from a group of compounds that are obviously closely related – the octahedrally built complexes; the phenomena of substitution orientation in aromatic compounds as a whole, and in five-membered heterocyclic compounds in particular; and so on).

He gives answers to a number of concrete critical remarks, and as I cannot agree that these answers are satisfactory and as I cannot regard the errors pointed out by me and admitted by Chelintsev as special cases, I am forced to continue my discussion of the "New Structural Theory".

The New Structural Theory is based on the recognition of two types of bond – "orbit" bonds and "contact" bonds. Orbit bonds, as described by Chelintsev, have not a single characteristic that distinguishes them from ordinary covalent bonds. Thus, orbit bonds differ from covalent bonds only in name. Hence, it is not these that lie at the basis of Chelintsev's theory. This is the part played by contact bonds. The latter "are subject to the rules of coordination numbers, of coordinaation, and of the octahedron".[1] "They are possible between coordinately unsaturated oppositely charged atoms, between coordinately unsaturated neutral atom-dipoles, and between the ones and the others, and here in the character of atom-dipoles we meet atoms with incomplete octets of valency electrons and atoms with unshared electrons in their valency shells. The main difference between charged atoms and atom-dipoles is that the former can form contact bonds directed towards all the corners of an octahedron (within the limits of their coordination numbers), while the latter form contact bonds only in directions corresponding to maximum and minimum electron density in their volumes. The coordination rule is the rule of opposite polarity of atoms in the direction of the contact bond".

---

[1] Here and later, the quotations are from Chelintsev's book [3].

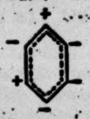
Contact bonds "are built by the deformative sharing by two atoms of electrons that are not orbitally shared". "The concept of the contact bond corresponds to the concepts of 'physical', 'ionic', 'electrovalent', 'ion-dipole', 'complex', 'molecular', and 'hydrogen' bonds."

"The concepts of orbit and contact bonds differ from the above-mentioned corresponding concepts in that the qualitative distinction between them and between either of them and Coulomb attractive forces (e.g., 'indirect' bonds with atoms in the second co-ordination zone) is expressed in their structures. Both orbit and contact bonds have not only attractive, but also combinational (deeper in the first case) significance and determine in a fundamental way the peculiar properties of the orbit- or contact-bond particles. Both orbit and contact bonds possess not only Coulomb (when they are polar), but also 'intrinsic' energies (more significant in the first case), being respectively — the energy of electron-orbit sharing ('exchange', 'resonance') and the energy of the deformative sharing of electrons; these determine the discreteness of the orbit- or contact-bond particles. Attractive forces act both between combined, and also between uncombined electrons, nuclei, and atoms, and these forces determine the properties of the particles to a considerable extent, but, in distinction to the bonds, they do not in any way determine the qualitative peculiarities of the molecules."

The central points of Chelintsev's theory are the postulation of homopolar contact bonds and the application of orbit-contact bonds to explain the properties of organic unsaturated, aromatic, and other compounds, in which the Butlerov theory of structure assumes a double bond. This ascribing to a contact bond of possible homopolarity is extremely important, as will be seen already from Chelintsev's "reply", since without this assumption the applicability of the New Structural Theory to the chemistry of unsaturated and aromatic compounds, i.e., to the greater part of organic chemistry, immediately disappears. With regard to the chemistry of saturated compounds — this is the field of orbit, i.e., covalent bonds, to which the New Structural Theory brings nothing new. Thus, without homopolar contact bonds Chelintsev's theory cannot exist.

Also, according to Chelintsev, the treatment of double bonds in aromatic and unsaturated compounds as containing the same sort of contact bonds that are characteristic for inorganic structures, which "are subject to the rules of co-ordination numbers, of co-ordination, and of the octahedron", leads to a unification from one single point of view of organic and inorganic chemistry. However, the only actual manifestation of the nature of the contact bond pointed out by Chelintsev in aromatic, unsaturated, or similar compounds (if we do not count homopolarity — for indeed it is not, according to Chelintsev, specific for the contact bonds, being, in fact, more characteristic for the orbit bond) was, before my critical review, the coplanarity assumed by Chelintsev for these structures, which was alleged to follow from the octahedral nature of the contact bond. That is why a withdrawal from this position, which undermines the unification of organic and inorganic chemistry on the basis of contact bonds with their identical properties for both fields, is not an exceptional, particular case for the New Structural Theory. What, after this withdrawal, has the "contact" bond in ethylene in common with the "contact" bond in common salt, the ion Hg$I_4^{=}$, or octahedral complexes? What we are talking about, of course, is something in common that stands in contrast to an orbit bond.

Neither is Chelintsev's error concerning an axis of symmetry of alleged third order in benzene to be considered as an exceptional case for his theory. The essential point about this mistake for the theory is not that the axis of symmetry of the crystal (which, at the same time, is given wrongly as an axis of third order) is used as an argument for the symmetry of the molecule of benzene. The essential point is that Chelintsev cited an axis of third-order symmetry for confirmation of his structural formula for benzene: From this it is clear what sense he attributed (at least, at the time when he wrote the book that I criticized) to the signs + and − that distinguish the adjacent carbon atoms of benzene in Chelintsev's formula. He now says that there is no distinction between the carbons, that his formula, as also the actual molecule, has sixth- and not third-order symmetry, that the contact bonds of benzene are homopolar, and that + and − denote not polarity, but the fact of the excess or deficit of an electron, as compared with the nuclear charge. But argumentation on the basis of an axis of third-order symmetry is a definite and convincing thing! It contradicts these assertions. Hence my criticism of Chelintsev's formula bracketed with the formulas of Vorländer and Berkenheim does not "miss the mark", but is right on the bull's eye. The withdrawal from the assumption of an axis of third-order symmetry in benzene which resulted from this hit is already a new point of view. Within the bounds of Chelintsev's theory it is inseparable from the postulate of the homopolarity of the contact bond. In his objections, Chelintsev attempts to give arguments in favor of what he himself calls the absurd concept of a homopolar electrovalent bond, as it would appear at a first glance [1]. The matter remains the same however, not only just at the first glance. So long as a contact bond is understood as an ionic bond, just as a covalent bond is equivalent to an orbit bond − all is in order. When in a molecule of ionic structure A^+B' we assume the polarization of the electron cloud of the anion by the cation, we again are concerned with methods of looking on these matters that are understood and have been applied for a long time in science.



If the atoms A and B are identical, then we may assume an unstable state $A^+ A'$. However, if we imagine polarization of the anion A' by the cation A^+ in such a way that the electron density will be distributed symmetrically about both A atoms (with a plane of symmetry perpendicular to the line A − A in its center), then the molecule would be homopolar, non-dipolar, but at the same time the electrons of the shell of the former anion A' would continue to belong to it and only to it, which means abandoning science and assuming purely juridical relations between the two A atoms. This is what is meant by a homopolar contact bond. Withdrawal from the axis of third-order symmetry and acknowledgement of an axis of sixth-order symmetry in benzene is significant in that it is an acknowledgement that these juridical relations leave no material trace in the molecule.

Is this really materialism? Is this not a manifestation of free will, if not of the electron, then of the nucleus? Have these "connective relationships" of electron and nucleus really got very far away from the life force? If it were not for these juridical relations, then with such a complete leveling-out of electron density, $A^+ A'$ would change into A − A with a covalent, or as Chelintsev wants to call it, orbit bond. Thus, the ability of a contact (i.e. electrovalent) bond to be homopolar, which is essential for Chelintsev's theory, is illusory and can in no way be justified by means of the examples cited by Chelintsev, such as nitrobenzene, with leveled-out electron densities around the two oxygen atoms,etc.

The above-mentioned juridical relations comprise, in fact, in this special case of electron and nucleus, the "connective relationships" that, according to Chelintsev, exist in the molecule in addition to the force relationships and, as far as one can understand his ideas, condition the specificity of chemical phenomena! Such a point of view, in my opinion, is indeed extremely similar to a recognition of a special life force, which is supposed to condition the specificity of biological phenomena. I do not doubt that Chelintsev ought to turn away from this point of view and so from the homopolarity of the contact bond (in other words, the non-polarity of the polar bond) together with all the consequences of this that arise in his theory.

As regards the point of view that I have expressed: although Chelintsev quotes my text correctly, he gives it a warped commentary. "The phenomenon of the discrete molecule, according to Nesmeyanov," he writes, "is completely embraced within the concept of an electron-nucleus aggregate, and the phenomenon of discontinuous change in the qualitative nature of molecules during reactions -- within the concept of the variation of the properties of molecules" [1]. I have said nothing from which such an inference could be made; it contradicts my assertion, cited by Chelintsev, that "... it does not follow at all that chemical phenomena should be reduced to physical and electrical, not to say mechanical phenomena..." [2]. I spoke of chemical reactions as "the conversion of one or several discrete particles (molecules), which possess definite qualities, into one or several other discrete particles (molecules) that possess new, different qualities...." [2], but Chelintsev in his commentaries tries to allege that I am of the opinion that the concept of chemical reaction is to be reduced to the concept of the changes in the properties of a molecule. What is this - lack of understanding by Chelintsev of the difference between the concepts of quality and of property, or a special method of discussion? How it is to be called I leave the reader to judge. I consider that this method is in the same category as the declaration that all critics, present and future, of one's own theory are Ingold-Paulingites.

A molecule is, of course, a nucleus-electron formation[1)], built up in a definite way[2)], and no special forces, other than the electron-nucleus interactions known to physics, take part in its build-up; but from this, in no sense should the inference be made, which Chelintsev wishes so much to ascribe to me, that the essence of a molecule is limited to this and that the essence of chemical change amounts to the redistribution of the nuclei and electrons of the reacting molecules. The essence of reaction, the essence of chemical movement, lies in the fact that from certain chemical substances as a result of reaction other chemical substances are formed, and this essence cannot be reduced to anything else, but constitutes the specific object of study of chemical science. Nevertheless, this essence of a higher (compared to physical and mechanical) form of movement has no need of any special mechanism, maintaining it and conditioning it, other than the known interactions of nuclei and electrons.

Indeed, for example, in this dispute between Chelintsev and myself, the essence is not in the mechanical movement of the pen over the paper, not in the muscular contractions that conditioned it, not in the biochemical and electrophysiological processes in the brain and nerves that preceded and accompanied these acts, and so on, but the thoughts that are expressed as a result of and through the means of these processes by each of us, thoughts that with respect to both their course and their mutual relations are subject to special laws. Our dispute, therefore, is in no way to be reduced to all the enumerated biophysical and biochemical acts, and others like them. But it would be an obvious idealistic fallacy to seek as a result some special discussion force or special discussion relationships between cells of the brain with which Chelintsev must

---

1) But not an aggregate, for an aggregate is a chance conglomeration, and a molecule is a strictly organized formation - a structure. Although Chelintsev saddles me with the word "aggregate", I have never used it.

2) E.g. in the sense of interatomic distances, energy levels, etc., but not in the sense of the presence of special mysterious properties in the nucleus and

be endowed in such great measure. In just the same way the essence of thermal movement cannot be reduced to mechanical movement, in spite of the fact that the latter must be placed at the basis of thermal movement. Thermal movement has its own peculiar laws, which are studied by thermodynamics. The concept of temperature cannot be applied to a single molecule and its movement. The second law of thermodynamics has no meaning for two or three molecules. Nevertheless, it would be absurd to seek some sort of special "thermal relationships" between these two or three molecules and to try to explain the laws of thermodynamics from these relationships. Similar considerations apply also to chemical change and its carrier - the molecule.

After all that I have said I may repeat that, if by "connective relationships" Chelintsev understands that specificity of a higher (than mechanical and physical) form of movement, which, indeed, forms the subject of the study of chemistry and is manifested, above all, in chemical reaction, then we have an obvious self-evident thing - a truism. If, however, by connective relationships is meant some specific force that stands outside the known physical interactions in the molecule or in the combination of nucleus and electron, then this, of course, means that we are on our way to the introduction into chemistry of the analog of life force. Unfortunately, Chelintsev's "reply" leads one to believe that he holds this second view. If this were not so, there would be no purpose in seeking "connective relationships" acting in the opposite sense to force relationships in the interaction of nucleus and electron, and those relationships of nucleus and electron (in a contact bond) that we have called juridical would not have been postulated. We will refer here to the quotation from Chelintsev's book that we made on p. 215; it gives a very clear illustration of what we have said (I will not go into Chelintsev's allegation that bonds have not only Coulomb energy, but also intrinsic energies ["exchange", "resonance"]). Thus, Chelintsev's whole conception is not "in accord with the philosophical meanings of the concepts of discreteness, discontinuity, quality, quantity, and property".

I will pass now to the remainder of my "particular" remarks that have been the subject of counter-objections on the part of Chelintsev. Chelintsev, in bringing forward his leveled-out formula for the CO_3'' ion, has in no sense disproved my arithmetic; his formula, like any other that takes into account the actual symmetry of the CO_3'' ion, expresses the fact that on each oxygen atom there is 1/3 of the charge of each of the two electrons of the anion and that an electron, therefore, is shared between more than two atoms. Only in this, indeed, consists the "delocalization" of which we are talking.

In his objections concerning the leveling-out of bonds in benzene, Chelintsev holds entirely to the idea of the homopolarity of contact bonds and to the ideas of the juridical appurtenance relationships of electron to nucleus, which leave no material trace. As regards this question, I refer the reader to p. 216.

Chelintsev writes further that the octet and tetrahedron rules exist independently of the New Structural Theory (this cannot be disputed - A.N.) and that no one has attributed to them the significance of general laws. This is not true. Such significance was attributed to them by none other than Chelintsev (see quotation on p. 215.) In fact, if Chelintsev had deduced the geometry of the contact bond not from octahedral complexes, but, for example, from the tetrahedral HgI_4'', then the result would be that (owing to the coincidence of the tetrahedral geometry of orbit and contact bonds) a tetrahedral configuration would have

---

electron, which compel the latter to remember that even when it is far removed from its master-nucleus and has come into the sphere of action of another nucleus, it still belongs to its master.

particular stability in olefins and aromatic compounds, which is an absurdity.

My criticism of Chelintsev relating to the prediction by his theory of the instability of benzene and the stability of the non-existent cyclobutadiene is not at all a misunderstanding, as Chelintsev supposes. In fact, Chelintsev brings forward arguments (as he now agrees - erroneous ones) to prove the planarity of aromatic structures from the postulate that the contact bond is built according to the octahedral principle, i.e. that the angle of four contact valencies is 90° (the same also for two) and that they lie in one plane. This means that, in his opinion, the geometry of the contact bond must actually determine the configuration of an aromatic system, and not the geometry of the orbit bond. From this it will be seen that my inference about the "prediction" and my criticism were altogether valid and logical.

If at that time Chelintsev had held the view expressed by him in his "reply" on p.210 to the effect that the valency angles of covalent bonds are more stable than the valency angles of electrovalent bonds, then he would not have made the inference of the planarity of benzene, due to contact bonds. Benzene would then have been like cyclohexane. The assertion that "the examples of the carbonate ion, the guanidine ion, the carboxyl ion, and the nitro group show that double orbit-contact (semipolar) bonds are arranged in one plane and form valency angles approximating to 120°" is nothing more than a statement of experimental fact, in no way derived from the "New Structural Theory", or from the geometry of orbit or contact bonds. This assertion can have only one relation with the New Structural Theory, that of an additional independent postulate. The necessity for the acceptance of this postulate by Chelintsev owing to the collapse of his explanation of the planarity of aromatic structures and of olefins has been pointed out by me in my "Reply to G.V.Chelintsev." [2].

Actually, the geometry of the contact bond - its construction according to the octahedron principle - has remained in force for Chelintsev, even after he has acknowledged his error in the explanation of the planarity of aromatic structures (this error has its basis only in the forgetting of the fact that two straight lines that intersect a third are not bound to lie in one plane). At least, he does not say anything about withdrawing this property of the contact bond.

It is doubtful whether there is any need to go into the remaining statements by Chelintsev in support of the New Structural Theory; they are equally unconvincing.

Objections to the postulates of the New Structural Theory will be removed only by the withdrawal of these postulates by their author. When Chelintsev renounces the unusual and unnatural properties of the contact bond, converts it into an electrovalent bond, expels it from unsaturated and aromatic structures, and replaces it in these structures by a double bond, with its propensity for being leveled out in conjugated systems, everything will be in its place. While this remains undone and the New Structural Theory differs (in the properties of the contact bond) from the old, this theory is bound to lead, at least in some respects, to conclusions that differ from those of the old theory, and they must be verified by experiment. I have pointed out some such conclusions that are in direct conflict with experiment. Chelintsev has withdrawn these conclusions together with certain properties of the contact bond, but it is essentially from these properties, taken as an associated whole, that the "New Structural Theory" is made up.

Our reproach to Chelintsev, that he himself refuses to make any inferences from his theory for verification by experiment, remains in full force. He is convinced, however, so he writes, that "the New Structural Theory and mesomerism-resonance theory did not come into being by virtue of their application to some newly discovered separate variety of particle that did not come within the scope of previous theories. In this sense, they cannot predict anything new" [1][1]. Comment, as they say, would be superfluous!

Under such conditions, our demand of G. V. Chelintsev that he should not only verify inferences made from the New Structural Theory by experiment, but should also attempt to predict some new facts on its basis is clearly excessive.

Our chemistry must be thoroughly cleared of all the unhealthy influences of corrupt bourgeois philosophy and science. It must be cleared also of vulgarization of home origin.

I do not doubt that by the joint harmonious efforts of Soviet chemists this will be done and that Soviet chemistry will develop still more widely and more brilliantly, utilizing in full our precious classical inheritance of Russian chemical science, the most recent results of chemistry and physics, and the great philosophy of Marxism-Leninism.

Received November 26, 1951

LITERATURE CITED

[1] G.V.Chelintsev. Bull.Acad.Sci.USSR, Div.Chem.Sci., 1, 190 (1952).

[2] A.N.Nesmeyanov. Bull.Acad.Sci.USSR, Div.Chem.Sci., 5, 542 (1950).

[3] G.V.Chelintsev. Notes on the Theory of Organic Chemistry. State Chemical Press, 1949.

---

[1] The emphasis is mine - A.N.

BLANK
PAGE

CHRONICLE

At the Academy of Sciences of the Armenian S.S.R. in Erevan on October 24-31, a conference was held on the problem of the relation between chemical structure and pharmacological activity as a basis for the search for new medicinals.

This conference, the first in our Union, was organized excellently by the pharmaceutical laboratory of the Academy of Science of the Armenian S.S.R., under the directorship of Corr.Mem. Prof. A.L. Mndzhoyan.

Scientific workers from Moscow, Leningrad, Sverdlovsk, Baku, and other parts of the Union attended the conference.

The large number of papers (more than 20) drew a big audience and called forth lively discussion, which considerably helped in the elucidation of very important questions that are exercising the minds equally of chemists, pharmacologists, physiologists, and clinical physicians. The absence of biochemists was noted with regret, and the conference resolved to take measures in future to bring clinicists and biochemists together in this work. The importance of the latter is very great for the solution of questions closely related to the properties of medicinals and to the role of the substrate of the organism, which directly reacts with the chemical compound.

The responsible role of clinicists in the characterization of medicinal preparations is beyond doubt, and their participation in the solution of the problem of the relation between chemical structure and biological action is quite essential in order to settle quickly the important question of the depositing of the chemical preparation in the treasure house of the pharmacopeia.

Of the large number of papers it is possible to note only a few that are of leading importance. As an introduction, a short historical sketch was given of the development of the pharmaceutical chemicals industry in our country.

Honored Scientist Dr. N.V.Lazarev gave the introductory paper on certain general questions in the study of the relation between structure and activity. Reg.Mem. Acad.Sci.USSR Kh.S.Koshtoyants gave an interesting and circumstantial account of his experimental physiological work concerning the significance of the sulfhydryl groups in the substrate of the living organism, and he emphasized particuarly the importance of I.P.Pavlov's teaching for the rational conduct of pharmacological investigations. Kh.S. returned to this theme on several occasions in his many speeches. "The Chemistry and Pharmacology of Choline-negative Agents" was treated in an illuminating paper by Prof. M.Ya.Mikhelson (Leningrad). Corr.Mem of the Academy of Medical Sciences Prof. V.M.Karasik (Leningrad) analyzed in detail the fundamental variants of the competitive interrelations between substances of similar chemical structure and behavior.

An interesting pharmacological paper was given by Prof. M.D.Mashkovsky (Moscow) on chemical structure and antihistamine activity; he considered that the utmost attention must be given to the importance and necessity of studying the pharmacological behavior of medicinals under test from every side.

The director of the pharmaceutical laboratory of the Acad. Sci. U.S.S.R., Corr. Mem. Prof. O. L. Mndzhoyan gave a circumstantial paper on the relation between chemical structure and anesthetic activity in organic compounds. In this paper, the review of original work in the Erevan laboratory is particularly valuable. This communication, and also interesting reports by the laboratory workers themselves, revealed the caliber of the young laboratory staff and gave every reason to believe that chemical work was being carried on at a high level in close contact both with local pharmacologists, and with many Leningrad workers.

A very important communication was made by Dr. (med. sci.) O. G. Birger (Moscow) on combined chemotherapy. As is well known, in the treatment of many diseases due to micro-organisms, sulfamide, antitubercular, and other preparations give rise to resistant strains of organisms, which are not susceptible to these drugs. Dr. Birger, giving many examples, showed that a good method of dealing with this troublesome phenomenon could be found in combined chemotherapy.

In a brilliant paper, Prof. Shamyakin (Moscow) examined in detail the question of the structure and biological activity of antibiotics. These compounds, which in a very short time have come to form a new important section of organic chemistry, were treated with exceptional lucidity and fulness.

Of the other chemical papers we may mention that of Prof. O. Yu. Magidson (Moscow) concerning the structure and chemotherapeutic activity of sulfamide preparations. Prof. Magidson is one of our greatest experts on this question and has done much valuable and original work in this important field, in which he has established the principal chemical regularities.

Other interesting papers were that of E. S. Golovchiskaya (Moscow) on derivatives of caffeine with various substituents in the 8-position and that of M. N. Shchukina (Moscow) on her very original investigations on the synthesis of antitubercular chemotherapeutical substances.

In connection with M. N. Shchukina's paper, we may mention also the interesting communication of V. G. Afrikyan (Erevan) on the chemical structure and antitubercular activity of certain amides.

It is not possible to enumerate all the interesting questions dealt with at the conference; they provide rich material on the fundamental question of the relation between chemical structure and biological activity in organic compounds. The conference noted also many short-comings in chemical work and pharmaceutical investigation and made valuable proposals for the elimination of great and small defects both in the scientific research institutes and also in other scientific and industrial organizations. Resolutions were carried unanimously relating to the necessity for carrying on scientific work on the basis of the teaching of Butlerov and Markovnikov, for paying greater attention to the study of the physical properties of organic compounds, and, in general, for carrying out the characterization of compounds more accurately and in greater detail in all respects. The pharmacological study of medicinal preparations must be carried on in the spirit of the fundamental theories of I. P. Pavlov, who laid down all the prerequisites for the creation of rational pharmacology and experimental medicine. A very important proposal was made by the conference concerning the setting-up of a general center for the co-ordination of all the organizations working on the problem of " chemical structure and activity", and it was decided to make a request to the Presidium of the Acad. Sci. U.S.S.R. concerning the organization of such a center.

The conference provided a large amount of material on the problem of "structure and activity", resolved to print the "Transactions of the Conference" as soon as possible, and proposed that a second such conference should be called in the near future to consider the question of structure and the biological activity of natural compounds.

CONFERENCE ON THE BASIC PROBLEMS OF PHOTOGRAPHIC SCIENCE

During the period June 29 - July 4, 1951 at Odessa, there was held an all-union conference on the basic problems of photographic science, organized by the Committee on Photographic and Cinematographic Science of the Div. Chem. Sci. of Acad. Sci. U.S.S.R. and by the I.I. Mechnikov State University of Odessa.

Participants in the conference included many representatives of our scientific institutes and of industry. Delegates and speakers came from several institutes of the Acad. Sci. U.S.S.R., from the Institute of Organic Chemistry of the U.S.S.R., from the Moscow State University, from the Odessa State University, from the All-union Research Institute for Cinematography and Photography, from the State Optical Institute, from the Leningrad Institute of Cine-engineers, from the factories and studios of the Ministry of Cinematography of the U.S.S.R., and from many other such places.

Opening the conference, the president of the Committee on Photographic and Cinematographic Science, Prof. K. V. Chibisov, pointed out that this was the sixth all-union conference on photographic science. The first three conferences took place before the Patriotic War - in 1932, 1937, and 1941. At the end of the war, the work of convening all-union conferences fell on the newly created Committee on Photographic Science of the Acad. Sci. U.S.S.R. Since then, three further conferences have been arranged - the fourth, at Moscow in 1949, at which the scientific and technical applications of photography and cinematography were considered; the fifth in 1950, also at Moscow, which was devoted to questions of photography and cinematography in color; and, finally, the present, sixth conference on the basic problems of photographic science, called in Odessa. The choice of place for the sixth conference was not an arbitrary one - Odessa, as the seat of the Physics Research Institute attached to Odessa State University, is one of the scientific centers of the photographic field. This center was built up by the work of a senior Soviet physicist, Prof. E. A. Kirillov, who set up a school of scientific work and for 25 years has directed the research institute referred to. In calling the conference in Odessa, the Academy Committee on Photographic and Cinematographic Science has marked the twenty-fifth anniversary of the founding of the Odessa State University Institute of Physics and has called attention to the valuable work of Prof. E. A. Kirillov and his scientific school.

An extensive discussion was made at the conference of three basic problems in photographic science, which lie at the basis of all photographic technology, including also cinematography: 1) the nature of photosensitivity and of the latent photographic image, 2) optical sensitization, and 3) the process of photographic development.

In discussions on the nature of photosensitivity and of the latent photographic image (three sessions), an important place was occupied by the work of E. A. Kirillov and his students (S. I. Golub, A. S. Fomenko, Zh. L. Broun, M. E. Fonkich, T. Ya. Serf, A. B. Kotlyarovsky, and others; papers were read by E. A. Kirillov, Zh. L. Broun, and M. E. Fonkich). In this work, which is of great interest for the theory of the latent image, it was shown that the absorption of photochemically and additively colored crystals of silver halide has a fine structure with a series of maxima over the whole region from 350 to 750 mμ. These maxima of light absorption closely correspond to the maxima of photoconductivity. It is interesting that the absorption maxima in the interval 450-540 mμ and at 600 mμ in the crystals of silver chloride, bromide, and iodide correspond satisfactorily, which points to the feeble influence of the crystal lattice of the basic material on the structure of the corresponding color centers. Analogous structures were found not only for free crystals but also for exposed silver bromide photographic emulsions. On the basis of these investigations it was concluded that, as well as colloidal particles, atomic centers and complexes of two, three, or more atomic centers exist in colored silver halide. The atomic centers, on increasing the exposure or the degree of dispersion of the silver, grow into colloidal centers. The centers that give rise to the fine structure are preserved even with exposures that produce intensive coloring. The spectrum of centers that are distributed within the crystal has an analogous structure, but with a different distribution of intensities. The absorption of a photographic emulsion that has not yet been exposed to light also has a fine structure. Thus, centers with which a fine structure is associated arise not only at all stages of the photochemical process, but also during the ripening of the photographic emulsion. Investigations were made also of the intensification of the latent photographic image under the action of light (Zh. L. Broun). It was found that a weak second exposure converts sub-latent centers into developable centers, while having little influence on the remaining particles of the latent image.

K. V. Shalimova discussed the nature of the centers of luminescence in silver halides. In this work an investigation was made of the luminescence of the chloride, bromide, and iodide of silver at the temperature of liquid air. The phosphors were obtained by sublimation of the respective silver salts. It was found that silver could be used as an activator of the luminescence. On the basis of the results obtained it was concluded that silver atoms are the source of the luminescence of silver halide phosphors containing both small and large amounts of activator. Further increase in the content of silver atoms in the lattice of the phosphor under the action of light leads to a state of the activator characterized by an absorption spectrum and absence of luminescence. This activator, which is in an unstable degenerate state, may be compared with the silver atoms that are feebly attached to the lattice of the crystal, the absorption of which was studied by E. A. Kirillov. The further formation of silver atoms under the action of light leads to the formation of colloidal silver particles, which give the absorption of color centers and do not show luminescence.

F. F. Volkenshtein reported on color centers in silver halide crystals and developed new ideas concerning the mechanism of the photochemical development of color in crystals and the physical nature of color centers. Attention was drawn to the fact that at the present time there is not sufficient evidence to enable a final choice of a model of an F-center to be made. The concept of Ya. I. Frenkel and Pohl, according to which an F-center is a silver atom (an electron near to an interstitial silver ion), and the concept of de Boer, according to which an F-center is an electron situated in a vacant anion space, have equal right to existence.

P. V. Meiklyar read a paper on the nature of the photochemical and photoelectric sensitivity of silver halide crystals and of the photographic layer. Comparison of the photoelectric sensitivity curves of silver halide with the spectral sensitivity curves of photographic layers of the same composition leads to the conclusion that the maximum of the spectral sensitivity curves in the blue-violet and near ultraviolet regions of the spectrum is determined by light absorption by F-centers (which in silver halide crystals are analogous in nature to the F-centers of alkali halide crystals). In silver halide crystals, F-centers may be formed not only by the action of light or heat, but also during the preparation of the emulsion and as a result of interaction of labile sulfur present in the gelatin with silver halide. The F-centers formed partially combine together to form centers of metallic silver. When the crystals in the emulsion absorb light, electrons are liberated both from F-centers and from halide ions. However, the F-center photo-effect plays a predominant part, since it occurs with a greater quantum yield.

An interesting paper on the relation between the systems of optical levels in ionic crystals and their X-ray absorption spectra was read by A. I. Kostarev. K. V. Chibisov reported on the untenability of Sheppard's theory of light-sensitive centers of silver sulfide. On the basis of his experimental results, obtained in conjunction with A. A. Mikhailov and A. A. Titov, he has concluded that the effect of chemical sensitization by sulfur compounds observed by Sheppard is not only inaccurately described, but is essentially incorrect, and hence the theory put forward by him in 1925 and widely accepted must be considered altogether invalid. As the lecturer showed, sulfur compounds accelerate chemical ripening only in so far as they are able to accelerate the reduction process, which has a direct effect on the changes in the photographic properties of the emulsion during the second ripening stage. As regards the mechanism of the acceleration of chemical ripening, the observed acceleration is evidently due to increase in the reactivity of silver ions in the crystal lattice near to the silver center, which results from the adsorption of "accelerator" molecules at bromide-ion sites.

I. M. Ratner, speaking for himself and on behalf of A. A. Titov, read a paper on the part played by internal centers formed when the emulsion is illuminated during ripening. The observed desensitizing action of internal silver centers agrees well with the earlier observation of K. V. Chibisov, A. A. Titov, and A. A. Mikhailov. The mechanism of this reaction is to be explained by the competition between internal and surface centers for the capture of photo-electrons. It was shown also that the formation of metallic silver by exposure of the photographic emulsion in the first ripening stage leads to diminished sensitivity only in the beginning stages, and with increased illumination the sensitivity is found to rise again. The results obtained are of fundamental importance for the understanding of the role of internal centers.

The properties of photographic layers that have been subjected to continuous illumination for varying times, or to periodic illumination, were the subject of a paper by A. L. Kartuzhansky. It was found that the laws observed for discontinuous illumination were basically similar to those observed for continuous illumination. At the same time, quantitative differences between the two effects and also a number of peculiarities observable with discontinuous illumination point to the existence of differences in the mechanisms of the two phenomena. These differences, as might be supposed, are connected with the fact that the process of latent-image formation continues also during the dark intervals.

In I. M. Roikh's paper, the question of the effect of hydrogen peroxide vapor on the latent image was considered. It was shown that, according to the exposure, the effect of hydrogen peroxide could be not only of an intensifying nature, but also of a reducing nature; this effect is evidently connected with the two ways (oxidizing and reducing) in which hydrogen peroxide can function.

The comparative effects of electrons and of light on photographic layers were treated by S. G. Grenishin. It is found that for a layer of low sensitivity to electrons the latent-image centers formed are similar to those formed by a short and intense exposure to light, whereas for a layer of high sensitivity to electrons the latent-image centers formed are similar in properties to those formed by prolonged and feeble illumination.

B. A. Barshchevsky read a paper on the quantum yield in photochemical and photo-electrical processes in silver halides, and he criticized the methods of calculating quantum yield used previously (Hilsch and Pohl, le Feld). In this paper, however, there were no convincing theoretical generalizations, and also no experimental data were cited.

Two sittings were devoted to discussion of problems of optical sensitization. A considerable proportion of the papers was concerned with the mechanism of optical sensitization. E. K. Putseiko, speaking on behalf of A. N. Terenin and of himself, read a paper on the sensitization by dyes of the internal photo-effect in semiconductors (ZnO, ZnS, TlCl, TlBr, TlI, AgCl). The condenser method, which permits the detection of the positions of local levels in the semiconductors and also the tracing of the accumulation of electrons in them, was used in this work. The semiconductors investigated have their own photoelectric sensitivity in the near ultraviolet and in the short-wave region of the visible spectrum. As a result of adsorption of dyes, photo-effect maxima appear in the visible region of the spectrum which cannot be attributed to dye microcrystals precipitated on the surface of the semiconductors and is due to adsorbed molecules. It was shown further that the photo-effect in the sensitization region shows a considerable temperature coefficient, whereas the sensitivity peculiar to the semiconductor itself changes insignificantly with temperature. It was shown also that the sensitizing effect (for TlI) depends on the concentration of F-centers in the semiconductor. Thus, the experiments show the possibility of electron exchange and accumulation of electrons in a crystal due to light absorption by molecules localized on its surface, which is a fact of great interest for the theory of optical sensitization.

Yu. N. Gorokhovsky reported on work that he had carried out in conjunction with B. V. Barbarin and E. I. Ozhereleva concerning the relation between adsorption of sensitizers, light absorption, and light-sensitivity in sensitized photographic layers. For the experiments, emulsion crystals, separated from photographic emulsions by fractional centrifugation, were used. It was found that the adsorption of the sensitizing dyes depends on the dimensions of the emulsion crystals (increases with decrease in dimensions), on the composition of the solid phase (increases on going from silver chloride, through bromide, to iodide), and on the duration of the chemical ripening of the emulsion. It was found also that the spectral sensitivity curves and the light-absorption curves for the adsorbed dyes (with the exception of erythrosine) coincided. It was concluded on the basis of the experimental results that the structure of the adsorbed layer depends not only on the initial state of the dye in solution, but also on changes in this state in the adsorbed layer, depending on the degree of adsorption. Work on the adsorption of sensitizers on pure silver bromide was reported by K. S. Lyalikov and Z. L. Petrushkina. It was shown in this work that a monomolecular layer of sensitizer is adsorbed irreversibly on silver bromide.

S. V. Natanson read a paper on the quantum yield of the sensitized photolysis of silver bromide. Quantum yields were determined for a number of dyes for wavelengths 436 and 578 mμ, which correspond to the sensitivity of silver bromide itself and to the sensitivity band of the molecular state of the dye in solution. It was found that the quantum yield of photolysis in the band of the intrinsic sensitivity of silver bromide is somewhat changed in presence of the dye, which does not absorb in this region of the spectrum. The quantum yield is the less, the stronger the tendency of the dye to show a desensitizing effect. Quantum yields of photolysis in the sensitization band bear a definite relation to the photographic efficiency of the dye.

A. V. Borin read a paper on the effect of gelatin on the absorption spectrum of a benzthiacarbocyanine dye. The dye showed a long-wave absorption band (I-band) and a short-wave absorption maximum (β-band). For various gelatins the intensities of these bands varied appreciably, and various fractions of gelatin obtained by fraction dissolution of gelatin in water differed in their effects on the two bands referred to. The relative intensities of these bands depended also on the interaction of the gelatin gels with the silver bromide surface (both pure and containing Ag_2S). The results obtained were interpreted in terms of interaction of the dye with gelatin molecules. Questions concerning the synthesis of optical sensitizers and the relation between structure and sensitizing propensity in dyes were examined in papers by E. D. Sych and I. I. Levkoev.

E. D. Sych, speaking on behalf of A. I. Kiprianov, made a report on the work of the Institute of Organic Chemistry of the Ukrainian S.S.R. Academy of Sciences on the synthesis of photosensitizers. The Institute has carried out a great volume of work on the synthesis of dyes of various classes. The investigations on dyes have revealed the great significance of steric hindrance in dye molecules with respect to its effect on color and other properties, including the sensitizing propensity of the dyes.

I. I. Levkoev lectured on the relations between structure and photographic activity in sensitizing dyes. Taking numerous examples of dyes synthesized in the laboratory directed by the lecturer, the dependence of the sensitizing properties of dyes on their structures was examined. The effect of substituents both in the nuclei and in the polymethin chain, the effect of the length of the polymethin chain, the structures of the heterocyclic nuclei, and so on were traced. The lecturer pointed out also the great importance of the basicity of the dyes for sensitizing effect (fogging action in the case of high basicity and desensitizing action in the case of low basicity). Also at the sittings devoted to optical sensitization, I. I. Breydo reported on the question of the effect of optical sensitization on the resolving power of emulsions.

Three sittings were devoted to problems concerning photographic development. G. P. Faerman gave two papers. The first of these, which was in the nature of a review, was devoted to the present state of the electrochemical theory of development. This theory, which has been developed systematically over a long period by the lecturer and his coworkers (S. G. Bogdanov, V. A. Veydenbakh, A. I. Kan-Kogan, S. I. Cherbov, and N. N. Shishkina) has succeeded in explaining a considerable number of facts concerning the relations between the properties of developers and their compositions and also certain questions relating to the mechanism of development. In the second paper, G. P. Faerman, on the basis of experiments carried out in conjunction with E. D. Vceykova, examined the mechanism of the catalytic action of development centers. On the basis of electrochemical concepts it was suggested that catalytic action in the development process would be shown by metals or by compounds that possess electronic conductance. Experiment has confirmed this suggestion for the reduction of silver nitrate by certain developing agents.

In S. G. Bogdanov and N. V. Polyakov's paper, the significance of the buffering action of the developing solution in the development process was considered. Experiments have shown that developers of similar composition, but with differing acid-base buffer reserve, do not behave in the same way in use, the developers with low buffer reserve having "leveling-out" properties. The work has shown also that the composition of the developer in the layer may, owing to exchange difficulties, be different from that in the outside solution, and this also is related to the buffer reserve of the developer, and it is of great importance for the results of development.

N. N. Shishkina read a paper on the dependence of the developing process on temperature. She showed that the fundamental postulates of electrochemical theory were applicable also in investigations on the dependence of development on temperature, in as much as they enable various developers, which guarantee constant results independent of temperature, to be made up by calculation.

K. S. Lyalikov, on his own behalf and on behalf of V. N. Piskunova, read a paper on a microphotographic investigation of the development process. The authors attempted to solve by this method the question of the part played by the solvent in the developer and to determine absolute rates of the growth of the silver crystal during development. The results obtained throw considerable doubt on whether reaction proceeds via the solution in normal chemical development. For the solution of the second question a statistical method of investigating the developed microcrystals of silver bromide was worked out. It was found that the development of the grain has an autocatalytic character, with a dwindling in rate, however, towards the end of the development of the grain.

V. I. Sheberstov read a paper on investigations into the kinetics of the development of photographic layers. It was shown that a unimolecular reaction equation can be applied satisfactorily to the rate of image development only in special cases when working with developers of high selective action. The development of fog often follows closely to a straight line law, which is to be explained by the formation of fog centers during development. In order to explain the experimentally observed dependence of development rate on time, the lecturer brought forward theoretical considerations that took into account the distribution of latent-image specks of varying activity within the grains and the autocatalytic character of the development of an individual grain.

N. M. Zyuskin read a paper on the dissolution of silver bromide in the course of photographic development. The experiments consisted in bringing silver images and photographic layers impregnated in developer into contact; the photographic layers were afterwards developed. Dissolution of silver bromide was to be observed in places in the photographic layer that had been in contact with the silver of the image, while the image was intensified in these places. This work points to the importance of diffusion processes and of the solubility of silver bromide in the development process.

All the papers gave rise to lively discussions.

When the work of the conference had been completed, a resolution was passed. In this resolution it was pointed out that deeper investigation into the essentials of the photographic process has not only permitted Soviet chemico-photographic, cinematographic, and optical industry to be brought to the technical level of the corresponding branches of industry of the large capitalist countries, and even into a leading place in individual questions, but also created the prerequisites for the further powerful development of these branches of industry. The progress of theoretical work in the photographic field in the U.S.S.R. is to be explained above all by the complex and planned character of the scientific investigations, which are carried out in close co-ordination with the demands of industry. The progress of theoretical investigations in photographic science results to an appreciable extent also from work done in allied branches of physics and chemistry.

The conference, in its resolution, took note of the very important problems that stand before workers in the field of theoretical photography:

1. Further study of the nature of the fine structure of the absorption spectra of photochemically colored silver halides, which was discovered by E. A. Kirillov and his coworkers. Development of work on the comparison of photochemical and photoelectric sensitivity in silver halides and the elucidation of the nature of color centers and of their relation to photographic sensitivity. Further development of investigations into the nature and origin of sensitivity centers in the crystals of photographic emulsions. Initiation of investigations into the photographic action of various radiations over a wide interval of wavelengths.

2. Carrying out investigations of the quantum yield in the regions of intrinsic and of sensitized sensitivity of photographic emulsions. Development of work both on the mechanism of optical sensitization and also on the sensitizability of photographic emulsions. Initiation of investigations directed toward the establishment of the relation between the structure of sensitizers, their physicochemical properties, and their sensitizing action.

3. Investigation of the mechanism of the catalytic action of silver in the development process. Study of the kinetics of the development both of separate emulsion crystals and of the photographic layer as a whole. Study of the effect of diffusion processes on photographic development. Investigation of the effects of various factors on the final results of photographic development.

Attention was drawn in the resolution to the delay in the publication of the transactions of conferences and discussions organized by the Committee on Photographic and Cinematographic Science. The conference found it necessary to recommend in the resolution that the Bureau of the Committee on Photographic and Cinematographic Science of the Academy of Sciences of the U.S.S.R. should again make a petition regarding the organization of a special journal on photographic and cinematographic science.

BLANK
PAGE

BLANK
PAGE

BLANK
PAGE

BLANK
PAGE

BLANK
PAGE

75th BIRTHDAY OF ACADEMICIAN E. V. BRITSKE

Highly respected and beloved Edgard Viktorovich!

The Division of Chemical Sciences of the Academy of Sciences USSR send you their best wishes on the occasion of your 75th birthday, and of the 50th anniversary of your scientific, pedagogic, and social activities.

It is difficult in this short greeting to enumerate all of your valuable contributions to the development of chemistry and chemical industry in our country. During these many years you have trained a very large number of chemists and engineers, who are now working productively in various branches of science and industry, among whom are to be found a number of academicians, associate academicians, and professors, who are worthily carrying on the work of their teacher.

As one of the active participants in, and organizers of, the Soviet system of scientific research institutes and industrial establishments, you made a great contribution to the industrialization of the Soviet Union, to the creation of its chemical industry, and to the realization of the Stalin Five-Year Plans. From the very beginning of the October Revolution up to the present day you have successfully held leading positions in scientific and scientific-technological organizations, and you worked actively in the Higher Soviet for National Economy and in the National Commissariat for Education. You took part in the creation of the basic chemical and fertilizer industries, and in the construction of a number of factories and mining establishments. You devoted much energy to the organization and management of the Institute of Applied Mineralogy and of the Institute for Fertilizers and Insecto-Fungicides. You were the first Academician-Secretary of the Division of Technical Sciences of the Academy of Sciences USSR, and you were the Vice-President of the All-Union Academy of Sciences. In your capacities, first of Professor of the Riga Polytechnical Institute, and then of the Plekhanov Institute of National Economics, and the Moscow Higher Technological School, you gave leadership to a vast school of industrial chemists. As a member of the All-Union Academy as well as of the V.I. Lenin Academy of Agricultural Sciences, you took part in the planning of research work, thus contributing to the development of the chemical and metallurgical industries and of agriculture.

Your scientific research work in the Institute of Metallurgy of the Academy of Sciences USSR led to the development and introduction into industry of new processes for treatment of minerals.

During the Great Patriotic War you displayed great administrative ability as the Vice-Chairman of the Commission for Mobilization of the Resources of the Urals for the Needs of Defense.

A characteristic feature of your activity is your constant effort towards linking theory with practice, and towards introducing science into industry.

Your extensive researches on the physical chemistry and improvement of methods of treatment of minerals, and towards finding new ways of processing natural phosphates and sulfur, arsenic, fluorine and other ores, and your profound studies of thermal processes and of physico-chemical properties of products, have led to the formulation of a number of theoretical rules applying to metallurgical and technological processes, based on the most recent advances in physical chemistry.

A thermal process for distillation of phosphorus from its ores, with the utilization of the gases and slags produced, was worked out on the basis of your discoveries, as were also a process for the complex treatment of titanomagnetites, and processes for the production of concentrated fertilizers and of arsenical insectofungicides.

The Government has valued your work very highly, awarding you a Stalin Prize, 1st Class, and a number of orders and medals.

The Division of Chemical Sciences of the Academy of Sciences USSR wishes you health, strength and long life, for the continuance of your creative work, which is directed towards the development of Soviet chemistry and technology, and towards the strengthening of the power, prosperity and culture of our great Fatherland.

Division of Chemical Sciences, Academy of Sciences USSR

PERIODIC LAW OF D. I. MENDELEEV AND THE STABILITY OF CO-ORDINATION COMPOUNDS

A. A. Grinberg and K. B. Yatsimirsky

One of us, when compiling the second edition of the monograph "Introduction to the chemistry of co-ordination compounds" [1], in 1950, considered the question of whether any connection exists between the position of an element in Mendeleev's periodic table and its ability to form co-ordination compounds. This study was based on a statistical treatment of the experimental material, and led to the following conclusions:

1. The tendency towards formation of co-ordination compounds is least in elements of Group O, and in elements of the immediately neighboring Sub-groups a of Groups I and VII (possessing the most stable electron shells).

2. The maximum tendency towards co-ordination compound formation is to be found among the elements of Group VIII (having the most labile electron shells, with unfilled d-levels). The elements of groups adjacent to Group VIII, are similar to these; this applies in particular to copper, silver and gold, which Mendeleev considered to be adjacent to the corresponding Group VIII elements, and to a smaller degree to elements of the zinc sub-group and to those of sub-group VII (b).

3. Thus, in the long periods, the capacity for forming co-ordination compounds is seen to be smallest at the margins, and greatest at the center.

4. The same applies basically to the short periods (Li ⟶ Ne) and (Na ⟶ Ar). The precise localization of the maximum is unlikely to be derivable from a statistical approach.

5. The "vertical" regularity found in the chief sub-groups appears to be that the power of functioning as a central ion is connected with a certain optimum range of values of "tension" of the ionic field. Very small values of this property are associated with an abrupt fall in the tendency towards complex formation. Very high values are associated with increase in the stability of the complexes with certain addenda (F, O), but the diversity of possible addenda is reduced.

It will be evident from the above that within sub-groups Ia and IIa the tendency towards complex formation falls with increasing atomic weight (volume) of the elements, whereas the reverse appears to apply to sub-groups a of Groups VII, VI, V and IV. Group III elements should occupy an intermediate position, which is particularly evident when this sub-group is considered together with the lanthanides.

The vertical regularity found in sub-groups b is less uniform. An important part is here played by the type of electron shell of a given element. It may be said, very generally, that there is a tendency within these sub-groups for complex-forming capacity to increase parallel with the atomic weight (copper, silver, gold; zinc, cadmium, mercury; gallium, indium, thallium; manganese, rhenium). The order in which the elements may be arranged may, however, vary according to the type of complex whose stability is being compared.

The above observations are, of course, only a first approximation to the answer to our problem, but even so they permit of the forecasting of the properties of a number of compounds. Bjerrum [2] attempted in 1950 to classify co-ordination compounds according to their stability in aqueous solution, on the basis of the periodic law, but his work is obviously of only very limited scope. Not only does this author confine his studies of complex-formation to aqueous solution, but he draws no conclusions regarding changes in the stability of the compounds along the periods, and says very little as to the nature of the stability variations within the groups.

It should also be noted that the parallelism noted by Bjerrum between the basic properties of addenda and their capacity for forming co-ordination compounds with ions of metallic elements has long since been pointed out by other authors. However, Chugaev [3] quite rightly said in 1906 that "the basic properties of amino-nitrogen, whether of diamines or of mono-amines, cannot be considered to be the sole factor determining the degree of stability of co-ordination compounds. It is evident that some other factor or group of factors, the nature of which is not yet known, is responsible*.

We shall in this communication attempt to clarify the connection between the periodic system and the capacity for co-ordination compound formation, based on a quantitative study of this property. The quantitative aspects considered will be the energy of formation of the gaseous complex ions, calculated according to Yatsimirsky's method [4] and also the instability constants.

The former magnitudes characterize the process of complex formation, in its pure form, so to speak. The latter characterize differences between the stability of a given complex ion and its corresponding aquo-ion. However, inasmuch as aqueous solutions represent the most important practical case, although only a particular one, the selection of instability constants as a measure of the stability of the compounds seems to be justified, both from the theoretical and the practical points of view.

The relation between the two parameters selected by us follows from the following considerations. It has been shown by one of us [5] that in reactions of co-ordination compound formation of the same type the change in entropy remains constant. Hence in such cases the heat of formation of a given compound in aqueous solution differs from the change in free energy associated with this process by some constant amount. The heat of formation of the complex in aqueous solution characterizes its stability, and we are justified in using thermochemical cycles for the evaluation of free energy changes.

Let us consider the following thermochemical cycle, for the process of formation of the complex ion $[M\,An]^{z+}$ from the central ions M^{z+} and $\underline{n}$ addenda A:

$$\begin{tikzcd}
\begin{array}{c}\text{Gaseous complex ions and}\\ \text{water molecules}\\ {[M\,An]^{z+}_{(gas)}};\ nH_2O\ (gas)\end{array} \arrow[r, "W_1-W_2"] & \begin{array}{c}\text{Gaseous aquo-ions and gaseous}\\ \text{molecules A}\\ {[M(H_2O)_n]^{z+}_{(gas)}};\ nA\ (gas)\end{array} \arrow[d, "-L_2-n\lambda A"] \\
\begin{array}{c}\text{Complex ions in aqueous}\\ \text{solution}\\ {[M\,An]^{z+}_{aq}}\end{array} \arrow[u, "n\lambda_{H_2O}+L_1"] & \begin{array}{c}\text{Simple ions in solution and}\\ \text{hydrated addenda}\\ M^{z+}_{aq}+nA_{aq}\end{array} \arrow[l, "\Delta H"']
\end{tikzcd}$$

L_1 and L_2 represent the heats of hydration of the ions $[M\,An]^{z+}$ and $[M(H_2O)]^{z+}$, respectively, W_2 and W_1 are the "addition energies" [4] of A and H_2O, respectively, to the gaseous ion M^{z+}; λ_{H_2O} is the latent heat of vaporization of water, and λ_A is the heat of hydration of the addendum A.

We obtain by summation of changes in enthalpy in all sections of the cycle

$$\Delta H = (W_1 - W_2) + (L_1 - L_2) + n(\lambda_{H_2O} - \lambda_A). \tag{1}$$

For reactions of the same type the last term is constant, and the penultimate one approximately so, whence

$$\Delta H \approx (W_1 - W_2) + \text{const.} \tag{2}$$

Taking into account the constancy of the difference between change in enthalpy and free energy, and the relation between the instability constant and the latter magnitude, we finally obtain the following expression:

$$RT\ \ln K \approx (W_1 - W_2) + \text{const}_1. \tag{3}$$

This expression shows that a direct connection exists between the instability constant and the energy of formation of gaseous ions. The instability constant is, as a first approximation, equal to the difference between the addition energies.

The experimental values given in Table 1 are in good agreement with those calculated from the expression.

Unfortunately, our quantitative characteristics cannot yet be applied to all elements forming co-ordination compounds, and to all types of compound formed by them. The reason for this is that on the one hand we possess approximately accurate numerical data for the energy of formation of gaseous complex ions for a few cases only (aquo- and ammino-ions), and on the other that we possess insufficient data relating to instability constants. Nevertheless, a study of this row has enabled us to arrive at certain quite interesting conclusions, applying in particular to elements of the subordinate sub-groups.

TABLE 1

Relation between energy of addition and the instability constant of complexes

Complex ions	Addition energy in kcal (W_2)	Addition energy for the hexa-aquo complex (W_1)	Difference between addition energies ($W_2 - W_1$)	Free energy of formation of the complex $\Delta Z = RT \ln K$	$W_2 - W_1 + \Delta Z =$ = const
$[Mg(NH_3)_6]^{2+}$	320 [4]	300 [4]	20	4.5 [6]	25
$[Co(NH_3)_6]^{2+}$	359 [4]	324 [4]	35	−7.0 [6]	28
$[Ni(NH_3)_6]^{2+}$	370 [4]	329 [4]	41	−11.9 [6]	29
$[Coen_3]^{2+}$	372 [4]	324 [4]	48	−18.8 [6]	29
$[Nien_3]^{2+}$	383 [4]	383 [4]	54	−25.3 [6]	29
$[Znen]^{2+}$	372 [4]	331 [4]	41	−16.4 [7]	25

We shall now proceed to compare :

(a) ions with an analogous structure of the outer electron shell, but with different charges and radii, and
(b) ions with identical charges, but with different structures of the outer electron shell.

The laws governing tendency towards co-ordination compound formation can readily be deduced for ions possessing an outer electron shell of the inert gas type (2 and 8 electrons); this refers above all to ions actually able to exist in solution, i.e., in general those having a charge of not more than 3^+.

Such ions (in particular, uni- and bi-valent ones) form complexes held together chiefly by electrostatic forces. The stability of the complex is here determined basically by the magnitude of the charge and by the ionic radius. For this reason, the heat of formation of such complexes varies parallel with the charge of the ion, and inversely with its radius

$$Na^+ < Mg^{2+} < Al^{3+}, \text{ etc.}$$

In accordance with the above, the stability of complexes falls with increase in the atomic number (from above down).

TABLE 2

Addition energies for hexa-aquo-ions and hexa-amino-ions of elements of Group II of the Periodic Table

Ions	Addition energies for ions of the types	
	$[M(H_2O)_6]^{2+}$	$[M(NH_3)_6]^{2+}$
Be^{2+}	–	411 [4]
Mg^{2+}	300 [4]	320 [4]
Ca^{2+}	257 [4]	237 [4]
Sr^{2+}	219 [4]	198 [4]
Ba^{2+}	–	171 [4]

The ions of this group do not characteristically form complexes with addenda which chiefly give rise to covalent linkings (Br^-, CNS^-, I^-, S_2O_3, CSN_2H_4 etc.). Complexes with addenda forming "intermediate" type linkings (NH_3, $C_2H_4(NH_2)_2$) are unstable. The ions of sub-groups a of Mendeleev's system yield complexes which are stable in solution, with addenda which are bound to the central ion basically by electrostatic forces (F^-, OH^-, O^{2-}, H_2O). As for ions with an inert gas type of electron shell, the stability of the complexes, in the gaseous state or in solution, rises from left to right in the periods, and falls from above down in the groups, since it depends basically on the charge and the radius of the ions. It may be expected that the stability of complex fluorides and oxy-ions of the higher valency "ions" of the right-hand side of the periodic system (such as P^{5+}, S^{6+}, Cl^{7+}, etc.), which are not encountered in the free state, should also rise from left to right along the periods, the dominating role of electrostatic characteristics being retained. Deviations from the rule may be expected here, however, owing to increase in the role played by covalent bonds as the charge increases.

The relative stability of complexes of this type should also fall from above down in the vertical groups. We emphasize that we are here speaking specifically of ions with an electron shell of the inert gas type; such ions as As^{5+}, Sb^{5+}, etc., are not considered here.

Substantially different rules are found for ions of elements of sub-groups b of Mendeleev's Table, with 18 electrons in their outer shell. Co-ordination compounds with predominatingly electrostatic bonds are not characteristic of this group, within which the binding forces between the central ion and the addenda are typically of a mixed nature. We find here that with the ionic type of bond, stability should diminish down the groups as the atomic number rises, whereas with the covalent type of bond the stability of the complexes should be at a maximum for elements of the 6th period (effect of ionization potential).

As a result of the summation of these oppositely acting factors it is often found that within sub-groups b the heats of formation of the corresponding gaseous ions fall initially, and then rise abruptly (Table 3).

TABLE 3

Addition energies for gaseous ammine-cations formed from elements of sub-groups b.

Complex ions	Addition energies	Complex ions	Addition energies
$[Cu(NH_3)_2]^+$	131 [4]	$[Zn(NH_3)_3]^{2+}$	366 [4]
$[Ag(NH_3)_2]^+$	104 [4]	$[Cd(NH_3)_6]^{2+}$	311 [4]
$[Au(NH_2)_2]^+$	160 [4]	$[Hg(NH_3)_2]^{2+}$	376 [4]

The same observation applies to the free energy of formation of the corresponding complexes in aqueous solution (Table 4).

The more clearly defined is the covalent nature of the bond, the more steeply does the stability of the complex rise, from above down (Table 5).

The data of Table 5 show that, for the case of iodides, the change in free energy of formation of complexes varies very abruptly in a vertical direction, but much less so in the case of chlorides; bromides occupy an intermediate position. It is of interest that increase in the charge of the central ion does not in this case lead to increase in the stability of the complex, but even to its slight diminution, at least in the cases studied (with the exceptions of Au^I and Hg^{II} bromides).

TABLE 4

Change in free energy in formation of complex ions in aqueous solution (ΔZ)

Central ions	Types of complexes					
	$[M(NH_3)_2]^{2+}$	$[M(NH_3)_4]^{2+}$	$[Men_2]^{2+}$	$[M(C_2O_4)_2]^{2-}$	$M(NH_2CH_2CO_2)_3^-$	$MN(CH_2CH_2NH_2)_3^{2+}$
Zn^{2+}	−6.55 [6]	−12.9 [6]	−14.1 [7]	−10.0 [8]	−16.5 [9]	−19.9 [10]
Cd^{2+}	−6.5 [6]	− 9.7 [6]	−13.6 [7]	− 7.9 [8]	−15 [9]	−16.7 [10]
Hg^{2+}	−23.8 [6]	−26.2 [6]	–	–	–	−31.0 [10]

TABLE 5

Change in free energy in formation of halide complexes

Complex ions	ΔZ = RT ln K	Complex ions	ΔZ = RT ln K
Chlorides			
$[CuCl_2]^-$	−7.54 [11]	$[ZnCl_3]^-$	− 0.20 [14]
$[AgCl_2]^-$	−7.70 [12]	$[CdCl_3]^-$	− 3.70 [15]
		$[HgCl_3]^-$	−19.0 [16]
Bromides			
$[CuBr_2]^-$	− 8.05 [11]	$[ZnBr_3]^-$	1.4 [14]
$[AgBr_3]^{2-}$	−14.0 [13]	$[CdBr_3]^-$	− 4.6 [15]
$[AuBr_2]^-$	−16.9 [11]	$[HgBr_3]^-$	−16.2 [16]
Iodides			
$[CuI_2]^-$	−12.00 [11]	$[ZnI_3]^-$	1.8 [14]
$[AgI_3]^{2-}$	−20.4 [13]	$[CdI_3]^-$	− 6.8 [15]
		$[HgI_4]^{2-}$	−41.3 [11]

Very little material is available relating to the stability of complexes formed from central ions having an 18 + 2 electron shell (Sn^{2+}, Pb^{2+}, Sb^{3+}, Bi^{3+}, etc.). The behavior of these ions in many respects resembles that of 18-electron shell ions, but there are also certain significant differences.

It is of considerable interest to compare the stability of complexes formed from central ions possessing an identical charge. It is here possible to follow the effect of the structure of the outer electron shell on the stability of the complexes, since in this case the radius of the ions remains approximately constant within a period (e.g., Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}, or Cr^{3+}, Mn^{3+}, and Fe^{3+}). The stability of complexes in which the ionic type of bond predominates (fluorides, phosphates, sulfates, etc.) is determined by the magnitude of the charge and by the dimensions of the corresponding ions, and for this reason such complexes are not very typical of uni- and bi-valent ions, but are highly characteristic of ions with charges of 3^+ or more. The stability of complexes having a type of chemical bond approached to the covalent one is determined by the magnitude of the ionization potential [4], which is connected with the structure of the outer electron shell.

The stability of the complexes rises from left to right along the periods (according to the increase in the number of d-electrons) to a maximum, and then falls abruptly, beginning with the element having 10 d-electrons (18-electron ion). The possibility of a fall in the complex-forming capacity of elements before the filling of the 18-electron orbit is not, however, excluded. This may occur when the given ions possess a well-marked oxidative action (Ni^{3+}, Cu^{2+}, Ag^{2+}, etc.). Increase in the redox potential is up to a certain limit associated with increase in the stability of the complex, but above this limit the central ion decomposes the addenda, by oxidizing them.

Table 6 presents changes in free energy associated with formation of a number of complexes of bivalent central ions. In all cases the stability of the complexes rises to Cu^{2+}, and then falls abruptly, starting with Zn^{2+}.

TABLE 6

Change in free energy (ΔZ) in formation of certain complexes in aqueous solution

Type of complex	Central ions					
	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
$[M(NH_3)]^{2+}$	–	–	− 2.9 [6]	− 3.70 [6]	− 5.65 [6]	− 3.22 [6]
$[M(NH_3)_4]^{2+}$	–	–	− 7.5 [6]	−10.82 [6]	−17.2 [6]	−12.90 [6]
$[Men]^{2+}$	−3.7 [6]	− 5.8 [6]	− 8.0 [6]	−10.20 [7]	−14.3 [7]	− 7.77 [7]
$[Men_2]^{2+}$	−6.5 [6]	−10.2 [6]	−14.6 [6]	−18.75 [7]	−26.6 [7]	−14.10 [7]
$[Mpn]^{2+}$	–	–	–	−10.1 [7]	−14.4 [7]	− 8.00 [7]
$[Mpn_2]^{2+}$	–	–	–	−18.7 [7]	−26.7 [7]	−16.65 [7]
$[M(C_2O_4)_2]^{2-}$	−7.3 [18]	–	–	–	−14.1 [17]	−10.0 [8]
$MN(CH_2CH_2NH_2)_3^{2+}$	−7.9 [10]	−11.7 [10]	−17.4 [10]	−19.9 [10]	−25.6 [10]	−19.9 [10]

A similar order is found for addition energy, i.e., for the heat of formation of gaseous complex ions from gaseous central ions and addenda (Table 7).

TABLE 7

Addition energy for gaseous ions [4]

Type of complex	Central ions									
	Ca^{2+}	Ti^{2+}	V^{2+}	Cr^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
$[M(H_2O)_6]^{2+}$	257	–	–	–	288	–	324	329	348	331
$[M(NH_3)_3]^{2+}$	237	–	–	324	314	337	359	370	388	366

The results described above may serve for the prediction of the possibility of existence and the stability of as yet uninvestigated complexes. Thus it may be supposed that the stability of complexes of the type $[M(C_2O_4)_2]^{2-}$, derived from the ions Fe^{2+}, Co^{2+}, and Ni^{2+} should increase from Fe^{2+} to Ni^{2+}, and that the free energy change associated with their formation should be within the limits −7.5 to −14 kcal. It may also be supposed that the addition energy for the hexa-aquo-ions of Ti^{2+}, V^{2+}, and Cr^{2+} should lie within the limits between 260 and 290 kcal., and the addition energies for hexa-ammine ions of Ti^{2+} and V^{2+} should be between 240 and 320 kcal.

The correlation of the stability of complexes with the place of the appropriate elements in the periodic table has thus permitted the formulation of certain generalizations, and the checking of experimental data, as well as the prediction of the stability of as yet unknown complexes.

Received July 20, 1951

LITERATURE CITED

[1] A.A.Grinberg. Introduction to the Chemistry of Co-ordination Complexes, 2nd ed. State Chemistry Press (1951).

[2] J. Bjerrum. Chem. Rev., 46, 381 (1950).

[3] L. A. Chugaev. Studies on Co-ordination Compounds. Moscow (1906).

[4] K.B.Yatsimirsky. Ann. Sector of Platinum, No. 25, 5 (1950).

[5] K.B.Yatsimirsky. J.Phys. Chem., 25, 221 (1951);

[6] J. Bjerrum. Chem. Abs., 6527 (1941); 3210 (1944).

[7] G.Carlson, I. Reinolds, and F. Verhock. J. Am.Chem.Soc., 67, 1334 (1945).

[8] V.C.Vosburgh and I.F.Beckman. J. Am. Chem. Soc., 62, 1028 (1940).

[9] E. Ferrell, J. Ridgton, and H.L.Riley. J. Chem. Soc., 1125 (1936).

[10] H. Ackerman, I.E.Prue, and G. Schwarzenbach. Nature, 163, 723 (1949).

[11] W. Latimer. Oxidation Potentials, N.Y. 1938.

[12] I. M. Korenman. J. Gen. Chem., 16, 157 (1946),

[13] W. Erber. Chem. Abs., 1947 (1943).

[14] L. G. Sillen and B. Liljegvist. Chem. Abs., 4588 (1946).

[15] H.L.Riley and V. Gallafent. J. Chem. Soc., 514 (1932); 1440 (1934).

[16] A. Johnson, J.Quarfort, and L.G.Sillen. Chem. Abs.. 2161 (1948).

[17] L. Meites. J. Am. Chem. Soc., 72, 184 (1950).

[18] R. W. Money, C.W.Davies. J. Chem. Soc., 400 (1934).

THERMOCHEMISTRY AND STRUCTURE OF ATOMS

PART 6. THERMOCHEMISTRY OF BORON: APPLICATION OF THE RULE OF THERMOCHEMICAL LOGARITHMICS TO ELEMENTS OF THE THIRD GROUP OF D. I. MENDELEEV'S SYSTEM

A. F. Kapustinsky and O. Ya. Samoilov

The increasing practical and theoretical importance of the chemistry of boron has attracted the attention of numerous research workers. Direct measurements of the heat of formation of boron oxide have been made, but the values reported by different workers differ considerably from each other. Roth and Borger [1], who combusted boron in oxygen, found that the heat of formation of the vitreous oxide was 349 ± 3 kcal, corrected by Roth in 1946 [2] to 339 ± 2.3 kcal. This value is in close agreement with that reported by Todd and Miller [3], viz., 335 ± 0.8 kcal, for spectroscopically pure boron. In 1949, however, Eggersgluess, Monroe, and Parker [4] repeated the work on direct measurement of the heat of formation of vitreous B_2O_3, which they found to be 281.1 ± 3.1 kcal. They ascribed the difference between their result and those of Roth and Borger and of Todd and Miller to contamination of the samples of boron with hydrides of boron.

Johnston, Hersch, and Kerr [5], in a paper devoted chiefly to the determination of the specific heat of elementary boron at low temperatures, derive the heat of formation of crystalline B_2O_3 (302.0 ± 3.4 kcal) from the summation of the thermal effects of five processes, including the heat of hydrolysis of diborane, which is, according to Roth and Borger [1] equal to 108.1 kcal.

Southard [6] determined the heat of dissolution of vitreous and crystalline B_2O_3 in water at 25° (1000 mole of water per mole of B_2O_3), finding values of 7.82 and 3.46 kcal per mole respectively. The heat of transformation of vitreous into crystalline B_2O_3 is thus 4.36 kcal per mole, according to Southard. According to Artsdalen and Andersen [7] the heat of dissolution of vitreous B_2O_3 in water at 25° (1110 mole of water per mole of B_2O_3) amounts to 7.928 ± 0.029 kcal per mole, and is only very slightly dependent on the final concentration of the solution. The value for infinite dilution is 7.960 kcal. per mole.

Only one value for the heat of formation of gaseous BCl_3 is known to us, viz., that of Troost and Hautefeuille [8], who in 1870 reported a value of 104 kcal. The heat of hydrolysis of gaseous BCl_3 (910 mole of water per mole of BCl_3) amounts, according to these authors, to 79.2 kcal per mole. Berthelot later found [9] that the heat of hydrolysis of liquid BCl_3 (650 mol of water per mol of BCl_3) at 10° is 65.8 kcal per mole, and that its latent heat of vaporization is 4.5 kcal per mole. According to Berthelot the heat of hydrolysis of gaseous BCl_3 is 70.3 kcal per mole. Roth [2] takes the heat of formation of BCl_3 as being 104 kcal.

We have determined the heat of hydrolysis of gaseous BCl_3, by a method depending on passing the gas through water at 25° in a calorimeter with an insulating envelope. Knowing the heat of hydrolysis of BCl_3 we can calculate from the heat of formation of B_2O_3 the heat of formation of BCl_3. As will be shown below, it is possible from this to arrive at the correct value for the heat of formation of boron oxide.

EXPERIMENTAL

The boron chloride in our possession was contaminated with chlorine, as was evident from its green color. It was purified with the aid of metallic mercury at 0°. The purity of the product so obtained was shown by the results of analysis of the solutions obtained in the calorimetric experiments; the mean molar ratio of HCl to H_3BO_3 in the solutions was 3.005, which corresponds with a purity of 99.87% for the BCl_3.

The heat of hydrolysis was measured in a calorimeter with an insulating envelope [10]. The envelope was kept at a temperature of 25° ± 0.01°. Hydrolysis was conducted in a glass calorimeter beaker of about 400 ml capacity. The experiments were performed as follows: the glass tube 5 (volume about 80 ml) is filled with BCl_3 vapor, and the tube is fitted into the circuit shown in Fig. 1. In the initial stage, air enters from a gasometer at 1, and is dried in the wash-bottles 2 and 3, containing sulfuric acid and phosphorus pentoxide, respectively, before going through the by-pass tube (tap 4 open, taps 6 and 7 shut) and the spiral 8, where it assumes the temperature of the thermostatic envelope of the calorimeter, and then through the injector 9 into the calorimeter water 11.

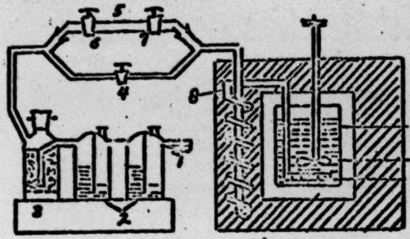


Fig.1. Diagram of apparatus: 1) entry of air from gasometer; 2) wash-bottles with sulfuric acid; 3) drying bottle containing phosphorus pentoxide on glass-wool; 4) tap of side-tube; 5) tube filled with boron chloride; 6 and 7) taps; 8) spiral; immersed in the thermostatic envelope of the calorimeter (diagonal shading); 9) a tube sealed at the end, with small openings for passage of gas; 10) a propeller stirrer; 11) calorimeter vessel containing water.

After completion of the initial stage of the experiment, tap 4 is closed, and taps 6 and 7 are opened, when the boron chloride in 5 is swept out into the calorimeter by a stream of dry air, entering the solution in the form of small bubbles, full absorption of which is facilitated by the action of the stirrer 10. The same amount (357 g) of bi-distilled water is taken in all cases. The final concentration of the solution amounted to about 6600 mol of water per mol of BCl_3.

The rise in temperature was measured by means of a Beckmann thermometer, calibrated by the All-Union Institute of Standards to an accuracy of 0.001°; readings were taken every 30 sec. The main period of the reaction lasted about 2-3 min. The rise in temperature amounted to 0.5-0.6°, and the rate of rise of temperature in the initial and final periods was 0.005-0.006° per min. Calorimeter corrections (for radiation, heat of vaporization of water, heat evolved by the stirrer) were calculated by the Regnault-Pfaundler-Usov formula, and amounted to 2-3% of the observed temperature rise. The method of determining the water equivalent of the calorimeter was the same as that previously described [10].

The solutions obtained were analyzed volumetrically, HCl by titration with NaOH, with methyl orange indicator, followed by titration of H_3BO_3 with phenolphthalein indicator after addition of mannitol [11]. Since the titrations of HCl were the more accurate, the number of moles of hydrolyzed BCl_3 was taken as being equal to one third of the number of moles of HCl formed. The accuracy of the final results for the heat of hydrolysis of BCl_3 is about 1.5%. The results obtained are given in Table 1.

TABLE 1

Results of experiments for determination of heat of hydrolysis of BCl_3
Water equivalent of calorimeter = 0.410 kcal per degree

Expt. No.*	Temp. rise in °C (corrected)	No. of Millimoles			$\frac{HCl}{H_3BO_3}$	Heat of hydrolysis in kcal per mole
		HCl	H_3BO_3	BCl_3		
1	0.521	8.007	2.723	2.669	2.94	80.0
2	0.594	8.895	2.965	2.965	3.00	82.1
3	0.634	9.696	3.221	3.232	3.01	80.4
4	0.561	8.535	2.789	2.845	3.06	80.8
						Mean 80.8

The heat of formation of BCl_3 can be derived from the heat of hydrolysis of gaseous BCl_3 so found:

$$BCl_{3(gas)} + 6603H_2O_{(liquid)} = H_3BO_{3\,(6600)} + 3HCl_{(2200)} + 80.8\ \text{kcal}.$$

Knowing the heats of formation of liquid water and $HCl_{(2200)}$*, which are 68 37 and 39.61 kcal, respectively [12], we obtain for the heat of formation of of gaseous BCl_3.

$$Q^{t}_{BCl_3} = Q_{H_3BO_3} - 167.1\ \text{kcal}. \qquad (1)$$

where $Q_{H_3BO_3}$ is the heat of formation of $H_3BO_{3(6600)}$.

According to Artsdalen and Andersen [7]

$$B_2O_{3(vitreous)} + 13203H_2O_{(liquid)} = 2H_3BO_{3(6600)} + 7.96\ \text{kcal}$$

and hence

$$Q_{H_3BO_3} = \frac{1}{2}Q^{t}_{B_2O_3} + 106.5\ \text{kcal}. \qquad (2)$$

---

* The figures in parentheses signify concentrations, expressed as moles of water per mole of dissolved substance.

where $Q^{g}_{B_2O_3}$ is the heat of formation of vitreous oxide.

We obtain from equations (1) and (2)

$$Q^{g}_{BCl_3} = \frac{1}{2} Q^{g}_{B_2O_3} - 60.6 \text{ kcal.} \tag{3}$$

The latent heats of vaporization and fusion of BCl_3 [12] [13], and the heat of transition of vitreous into crystalline B_2O_3 [6], are equal, respectively, to 5.68, 0.50, and 4.36 kcal per mol. It hence follows from equation (3) that:

$$Q_{BCl_3} = \frac{1}{2} Q_{B_2O_3} - 56.6 \text{ kcal,} \tag{4}$$

where Q_{BCl_3} is the heat of formation of crystalline BCl_3, and $Q_{B_2O_3}$ is the heat of formation of crystalline B_2O_3. Equation (4) relates the values of Q_{BCl_3} and $Q_{B_2O_3}$. In this way the determination of the correct value of the heat of formation of B_2O_3 is of importance for the determination of this constant for boron chloride.

Apart from Johnston, Hersch, and Kerr's [5] indirect derivation of $Q_{B_2O_3}$, there are three direct, and hence preferable, determinations of this value, as has been mentioned above [2], [3], and [4]. The first two of these are in close agreement, being 343.4 and 339.4 kcal (for crystalline B_2O_3); the mean value 341.4 kcal may be taken to represent both. The third value (285.5 kcal) is nearly 20% lower than the above mean value. Inasmuch as all three determinations appear to have been performed with equal accuracy it is not possible to decide which of the results to accept, without subjecting them to a theoretical analysis. We shall in the following section of this paper describe the way in which the selection of the correct values of heats of formation can be made.

THEORETICAL

According to the rule of thermochemical logarithmics, heats of formation, related to a single bond $\left(-\frac{\Delta H}{W}\right)$, are linear functions of the atomic number Z of elements. Within each group or period of the periodic table this holds for isoelectronic analogs [14] in the absence of "inversion points" (ρ), which may be established by crystallochemical data [15]. The application of the above-mentioned rule to the cross-checking of the basic thermochemical properties of compounds of Group III elements is of importance to the choice of the correct value of two possible values for the heat of formation of boron chloride. It would seem, however, that we here encounter very real difficulties, as appears from Table 2 and Fig. 2.

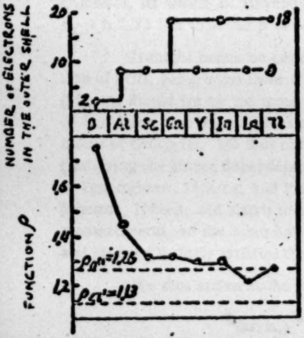


Fig. 2. Diagram of properties of ions of elements of Group III

TABLE 2

Properties of ions of Group III elements

Element	B	Al	Sc	Y	La	Ga	In	Tl
Atomic No. Z	5	13	21	39	57	31	49	81
No. of outer electrons of the cations	2	8	8	8	8	18	18	18
Function ρ	1.75	1.44	1.31	1.29	1.21	1.31	1.29	1.26

The cations of Group III elements fall into two "classes": the ions possess an inert gas or an 18-electron shell, and in the former class the outer electron shell varies from 2 electrons for boron to 8 electrons for the others. In addition, the phenomenon of "inversion" should be observed in the case of the oxides.

It has been noted [14] that elements placed at the beginnings of groups deviate systematically from the rule of thermochemical logarithmics, and that the deviation is the greater the further is the group from the center one (Group IV). This interesting feature of the periodic system is fully explicable on the basis of modern conceptions of atomic structure. The atoms of the elements of any Group of the periodic system may be regarded as electronic analogs, in the case of the elements themselves, or of their covalent compounds. However, their ions are not complete electronic analogs, but only to the extent that they possess an identical architecture of their electron shell. Thus, for example, B, Al, Sc, Y, La, Ga, In, and Tl should, using Nekrasov's terminology [16], be regarded as being analogs, from the electronic standpoint (they all have 3 valency electrons), whereas in the form of ions only B, Al, Sc, Y, and La can be regarded as analogs, since they have an inert gas type of orbit, and are distinct from the 18-electron orbit ions Ga, In, and Tl, which are analogous to each other. But even the inert gas ions are not entirely uniform, since B gives a 2-electron cation, whereas the Al, Sc, Y, and La cations are 8-electron ones.

The further from the middle of the periodic system is the given group, and correspondingly the more clearly defined is the ionic nature of the bonds, the more distinctly will this difference in the structure of the inert gas ions appear. Thus, for example, in Group I the properties of lithium differ considerably from those of the other alkali metals, while in Group II the properties of beryllium differ much less from those of other elements of this group, being scarcely distinguishable in the case of the carbonates, and, finally, the elements of Group III show very uniform properties, boron scarcely differing from the other elements of this group in the general gradation of properties.

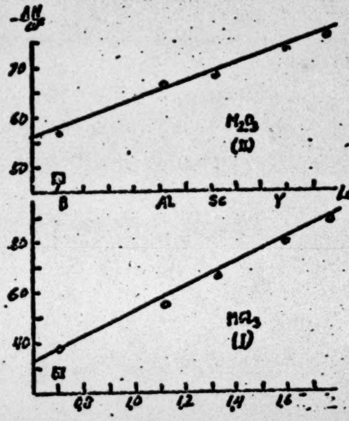


Fig. 3. Heat of formation of chlorides and oxides.

This explanation may also be based on quantitative data, using estimates of the "ionicity" of bonds, derived from electro-negativity measurements [17]. In the chlorides series this amounts to 60% for LiCl, to 40% for $BeCl_2$, and to 20% for BCl_3. It is to be expected that if the ionic type of bond dominates among the alkali chlorides, the difference between lithium and its analogs will depend on the differences between the electronic structures of the ions. For the first elements of Group III, however, it is resemblances between atom-analogs, rather than ion-analogs, which dominates, since the share of ionic forces is only 20%. Differences between inert gas type ions are no longer clear-cut; only the more definite differences between these ions and ions with an 18-electron orbit* remain. For this reason boron should not give deviations from the rule of thermochemical logarithmics; this conclusion should at any rate be applicable to the chlorides, for which an "inversion point" does not exist: ρ_{Cl}, is 1.13 less than the ρ of all the cations of Group III.

It might hence be concluded that the heat of formation of BCl_3, per g-equivalent within the given coordinates (Fig. 3), should lie on the same straight line as do the heats of formation of other chlorides of inert gas type ions of elements of Group III. We thus obtain a criterion for judging which of a number of values advanced is the correct one (satisfying the linear dependence of $-\Delta\underline{H}/\underline{w}$ on ln $\underline{Z}$). We see from Fig. 3 that $-\Delta\underline{H}/\underline{w}$ for BCl_3 as derived from the data of Eggersgluess, Monroe, and Parker [4] (crossed square) is inacceptable. The mean value ($-\Delta\underline{H}/\underline{w} = 31.4$) derived from Johnston, Hersch, and Kerr's results [5] is also doubtful, although it is not so far off the line. The value given by our measurements, on the other hand, considered together with the values of $\Delta\underline{H}_{B_2O_3}$ obtained by Roth [1, 2] and by Todd and Miller [3], fully satisfies the criterion required above; the point lies on the curve.

We thus arrive at the following final results for the thermal effect of the reaction (in kcal per mole):

$$B_{(cryst.)} + 3/2\ Cl_{2(gaseous)} = BCl_{3(cryst.)},\ \Delta\underline{H}_{298} = -114 \pm 3$$

or

$$B_{(cryst.)} + 3/2\ Cl_{2(gaseous)} = BCl_{3(gaseous)},\ \Delta\underline{H}_{298} = -108 \pm 3$$

But, since the above value contains within it also the $\Delta\underline{H}_{298}$ for B_2O_3 (cf. equation 4), we arrive at the conclusion that the results of Roth, and of Todd and Miller must be correct. They are practically identical, so that taking the mean (56.7 ± 0.2 kcal per g-equiv.), we obtain the following as the most reliable value:

$$2B_{(cryst.)} + 3/2\ O_{2(gas)} = B_2O_{3(cryst.)},\ \Delta\underline{H}_{298} = -341 \pm 3 \text{ kcal/mole}$$

---

* The "ionicity" of the bond rises with increase in the atomic number of elements within each group.

or

$$2B_{(cryst)} + 3/2\,O_{2(gas)} = B_2O_{3(vitreous)},\ \Delta \underline{H}_{298} = -337 \pm 3 \text{ kcal/mole.}$$

It follows from Fig. 2 that the inversion point for oxides of Group III elements appears only at the end of the group, and this cannot lead to the appearance of an inflexion in the $-\Delta \underline{H}/w$ ln $\underline{Z}$ curve. The rule of thermochemical logarithmics should hence be followed here over the whole range. This is confirmed by Fig. 3 (II), which thus affords yet another proof of the correctness of our conclusions.

Although the part of Johnston, Hersch, and Kerr's work dealing with the heat of formation of B_2O_3 cannot, as we have shown, be considered to be acceptable, their entropy determinations must be considered to be wholly acceptable, without any reservations. Combining these results with those presented in the present paper we arrive at the following values for standard free energy, in kcal per mole:

$$2B_{(cryst.)} + 3/2\,O_{2(gas)} = B_2O_{3(cryst.)},\ \Delta \underline{F}_{298} = -322 \pm 3$$

or

$$2B_{(cryst.)} + 3/2\,O_{2(gas)} = B_2O_{3(vitreous)},\ \Delta \underline{F}_{298} = -318 \pm 3$$

We wish to express our gratitude to L. C. Morozov for a supply of boron chloride, and to I. I. Lipilina for helping in the experimental work.

SUMMARY

1. The heat of hydrolysis of gaseous boron chloride has been determined.

2. Applying the concepts of electronegativity, of degree of ionicity of bonds, and of the function (see our previous communication) it has been shown that inversion cannot take place in the heats of formation of the series of chlorides B, Al, Sc, Y, and La, but that the rule of thermochemical logarithmics should be observed here. This allows of the derivation of the following values for heat of formation of BCl_3 (kcal per mole):

$$B_{(cryst.)} + 3/2\,Cl_{2(gas)} = BCl_{3(cryst.)},\ \Delta \underline{H}_{298} = -114 \pm 3$$

or

$$B_{(cryst.)} + 3/2\,Cl_{2(gas)} = BCl_{3(gaseous)},\ \Delta \underline{H}_{298} = -108 \pm 3.$$

3. The experimental values found for the heat of hydrolysis of BCl_3 show that the correct value for its heat of formation is in accordance with the expression

$$2B_{(cryst.)} + 3/2\,O_{2(gas)} = B_2O_{3(cryst.)},\ \Delta \underline{H}_{298} = -341 \pm 3.$$

This confirms the work of Roth and Todd and Miller, but not of Eggersgluess, Monroe, and Parker, and also shows that the results calculated indirectly by Johnston, Hersch, and Kerr for the heat of formation of B_2O_3 are wrong.

4. Combining the measurements of specific heat (entropy) given by these authors with the results presented in the present paper, the following figure can be derived for the free energy of formation of boron oxide (kcal per mole:

$$2B_{(cryst.)} + 3/2\,O_{2(gas)} = B_2O_{3(cryst.)},\ \Delta \underline{F}_{298} = -322 \pm 3$$

5. The rule of thermochemical logarithmics is followed without exception by the chlorides and oxides of the elements of Group III of the periodic system.

LITERATURE CITED

[1] W. Roth, E. Borger, A. Bertran, Ber., 70, 48, 971 (1937).

[2] W. Roth, Z. Naturforsch., 1, 574 (1946).

[3] J Todd, R. Miller, J. Am. Chem. Soc., 68, 530 (1946).

[4] W. Eggersgluess, A. G. Monroe, W. G. Parker, Trans. Farad. Soc. 45, 661 (1949).

[5] H. Johnston, H. Hersch, E. Kerr, J. Am. Chem. Soc. 73, 1112 (1951).

[6] J. Southard, J. Am. Chem. Soc., 63, 3147 (1941).

[7] E. Van-Artsdalen, K. Andersen, J. Am. Chem. Soc. 73, 579 (1951).

[8] L. Troost, P. Hautefeuille, Comptes rend., 70, 185 (1870).

[9] M. Berthelot, Ann. chim. phys. [5], 15, 215 (1878).

[10] A. F. Kapustinsky and O. Ya. Samoilov. Bull. Acad. Sci. USSR, Div. Chem. Sci., 4, 337 (1950).

[11] G. Basset Theory of quantitative analysis. Leningrad, 1932.

[12] E. V. Britske, A. F Kapustinsky, et al. Thermal constants of inorganic substances. USSR Acad. Sci. Press, [illegible], Moscow-Leningrad, 1949.

[13] L. Brewer, The fusion and vaporization data of halides, in the collection "The Chemistry and Metallurgy of Miscellaneous Materials", L. Quill, 1950.

[14] A. F. Kapustinsky. Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 6, 568, 581 (1948).

[15] A.F. Kapustinsky and Yu. M. Golutvin. Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 1, 3 (1951).

[16] B. V. Nekrasov. Text book of General Chemistry, Moscow-Leningrad, 1948.

[17] L. Pauling. Nature of the chemical bond. Moscow-Leningrad, 1947.

Received July 16, 1951

N.S. Kurnakov Institute
of General and Inorganic Chemistry
of the Academy of Sciences, USSR

MICRO-HARDNESS METHOD OF STUDYING INTRACRYSTALLINE LIQUATION

D. A. Petrov and L. A. Raikovskaya

1. NATURE OF THE PHENOMENON OF INTRACRYSTALLINE LIQUATION

Intradendritic or intracrystalline liquation of alloys is the term applied to non-uniformity of crystals of solid solutions of metals due to irregular distribution of their constituent parts during solidification. This non-uniformity is connected with disturbances of equilibrium taking place during crystallization as a result of retardation of diffusion processes due to excessive velocity of solidification.

The theoretical aspects of this problem have been discussed in detail by one of us [1], and we shall here repeat only the basic propositions. The crystallization of solid solution from the melt is shown by the phase diagram in the following way. As a liquid of composition $\underline{c}$ cools it becomes saturated with respect to crystals of solid solution at temperature $\underline{t}_1$ (Fig. 1), and crystallization begins with further fall in temperature. The composition of the crystals separating initially is represented by the point $\underline{c}_1'$ on the phase diagram. As cooling proceeds, the composition of both phases changes continuously, of the liquid phase along the liquidus curve, and of the solid solution along the solidus curve. The alloy finally solidifies at $\underline{t}_4$, with formation of a homogeneous solid solution, the composition of which from now corresponds with that of the alloy.

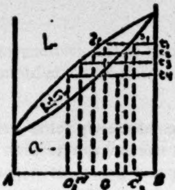


Fig. 1. Scheme of crystallization of solid solution under equilibrium conditions.

Since the composition of the solid solution does not remain constant, but changes continuously as crystallization proceeds, the conversion of the liquid into solid solution should be regarded as two parallel processes:

a) Actual formation of crystals of solid solution at temperature $\underline{t}$ (Fig. 2):

$$L_t \longrightarrow \alpha_t$$

b) Change in composition of crystals formed at higher temperature $\underline{t}$ + dt (Fig. 2):

$$L_t + \alpha_{t+dt} \longrightarrow \alpha_t$$

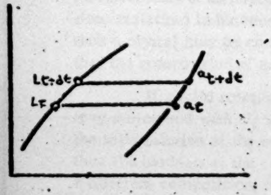


Fig. 2.

The former process assumes diffusion only in the liquid phase, and it proceeds readily in molten metals. The latter process assumes diffusion to take place also in the solid phase, and this process is a slow one, becoming increasingly more difficult the lower the temperature. Diffusion in the solid phase may be completely abolished at high speeds of cooling, and at even higher speeds the same may apply to the liquid phase as well. We shall not here consider this case, but shall assume that diffusion proceeds without hindrance in the liquid phase. In the absence of diffusion in the solid phase the solid solution forming will not be a uniform one, but will represent an unbroken series of compositions, beginning with composition $\underline{c}_1'$ on Fig. 1.

The question arises, what will be the final term of this series of compositions ? In other words, at what temperature will solidification of the melt be completed, in this case? In the absence of diffusion in the solid phase the second of the above processes associated with conversion of liquid into solid solution, i.e., the change in composition of the solid solution

$$L_t + \alpha_{t+dt} \longrightarrow \alpha_t$$

does not take place at all. As a result, all the liquid which would under equilibrium conditions have entered into this process remains unsolidified at temperature t_4 which corresponds with completed crystallization of the alloy according to the phase diagram (Fig. 3).

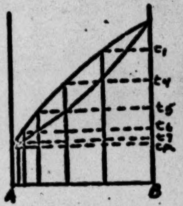


Fig. 3. Scheme of crystallization of solid solution under non-equilibrium conditions.

In considering the process of crystallization of this part of the solution, beginning with temperature t_4, we similarly arrive at the conclusion that at temperature t_5 there will still remain unsolidified a certain part of the metal which was liquid at t_4, and at temperature t_6 some of the residual liquid from t_5 will still remain unsolidified, and so on. It follows that solidification of the melt will be completed only at the melting point of component A.

Reverting to the question of the non-uniformity of crystals of solid solution, we hence see that the degree of intra-dendritic liquation at high speeds of cooling is determined by the concentration interval between the composition of the initially forming crystals and the pure component with the lower m.p. It can, furthermore, be readily shown that in systems forming eutectic mixtures of solidification solutions of all alloys, in absence of diffusion in the solid phase, is completed at the eutectic temperature. The eutectic will, under these conditions, appear when even the least amount of the second component is added. In that case, the degree of intra-dendritic liquation, at high speeds of cooling, will be determined by the concentration interval between the composition of the initially formed crystals and of the crystals of solid solution saturated at the eutectic temperature.

2. EXPERIMENTAL

Intracrystalline liquation was studied for alloys of aluminum with magnesium, and of bismuth with antimony. One of the methods used was that of measurement of micro-hardness, recommended for the study of non-uniformity of crystals by Bochvar and Zhadaeva [2].

Micro-hardness was measured by means of a diamond micro-indentor, which gives indentations of the order of 10 μ^2 cross-section. With a grain size of the order of 10^3 μ^2 (on polished surfaces) this indentor permits of hardness measurements at different parts of a single crystal. If the crystal is not homogeneous, owing to intra-crystalline liquation, variations in hardness are to be expected at different parts of the cross-section of the crystal. The formation of such a crystal may be considered as resulting from deposition of successive layers on the original crystal nucleus, so that the composition of the grain changes continuously from the center to the periphery.

If a solid solution of composition c (Fig. 4) crystallizes, the composition of the central part of the grain formed may correspond with c', while that of the peripheral zones of the grain will be c_1, i.e., that of the saturated solution of the solid solution at the eutectic temperature. If the line abd represents changes in the hardness of equilibrium alloys, then the hardness at the center of the grain will correspond to H_1, and at the periphery to H_2 (Fig. 4). For an alloy of a different composition, such as, for example c_1, the composition at the center of the grain will be c_1', and the hardness H_1', and the composition at the periphery will be c'', and the hardness H_2, as for the previous alloy. It is evident that with change in the content of the component B in the alloy, the composition of the center of the grain will change gradually, in the direction A → B, approaching c°, whereas the composition of the peripheral zones of the grains will remain the same for all alloys.

At the same time the hardness of the center of the grain will rise with increasing content of B in the alloy, according to a curve such as Curve 1, Fig. 4, whereas the hardness of the peripheral zones will lie on a horizontal line (Curve 2, Fig. 4). The curves approach each other as the content of B increases, until they intersect at a point corresponding with the composition of the eutectic alloy. In other words, differences in the composition, and hence in the hardness, of the center and the marginal zones of the grains, are the most marked in the case of alloys with a low content of B, and then gradually diminish until they vanish altogether in the case of eutectic alloys. The grains of solid solution separating from the eutectic alloy are of a uniform composition, irrespective of the rate of cooling. All values of hardness found at all parts of cross-section of grains are included between the two curves.

Alloys of antimony with bismuth (0 – 90% of Bi, at intervals of 10%) and of aluminum with magnesium (0, 1, 4, 8, 12 and 16% of Mg). The Sb-Bi alloys were cooled in an oven, and the Al-Mg alloys at room temperature, i.e., they were cooled comparatively slowly, so as to obtain fairly large grains. For air-cooled alloys the crystallization interval was 5-10 min., as compared to 20-30 min. for oven-cooled alloys. The largest grains present in the alloys were taken for hardness measurements, in order to obtain as full a picture as possible of distribution of hardness within single crystals.

The results of the measurements are shown in the diagrams Figs. 5 and 6. The length of the diagonals of the indentations in microns is given in the upper parts of the diagrams. The number of dots recorded against each composition represents the number of indentations made. The points on the same horizontal line all have the same size of indentation. Curves are drawn through the points corresponding with maximum and minimum values of diagonals of indentations. The lower parts of the diagrams give microhardness curves, derived from the values for the diagonals; the upper curves represent maximum values for hardness of solid solutions, taken from the results obtained for a number of grains of a given alloy, and the lower curve expresses minimum values obtained similarly. All intermediate values for hardness of grains lie between these two curves.

The diagram for Al-Mg alloys (Fig. 5) resembles the theoretical diagram, with the difference that the upper curve becomes rectilinear only above 4% of Mg. The difference between maximum and minimum hardnesses is greatest for alloys with 4% of Mg, being much smaller for alloys with 1% of Mg. This is evidently due to the circumstance that the degree of intra-crystalline liquation does not, at the rate of cooling applied to these alloys, attain a sufficiently high value to cause total suppression of diffusion in the solid solution. The lower curve rises smoothly, as was to be expected (cf. Fig 4). The eutectic point, at which the two curves of the system should intersect, is at about 34% of Mg, outside the limits of this diagram.

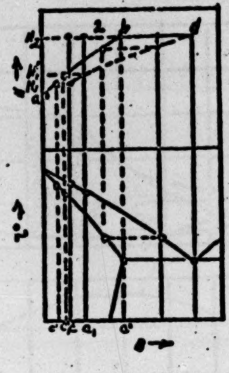


Fig. 4. Scheme of change of hardness within grains of solid solution under conditions of intra-crystalline liquation.

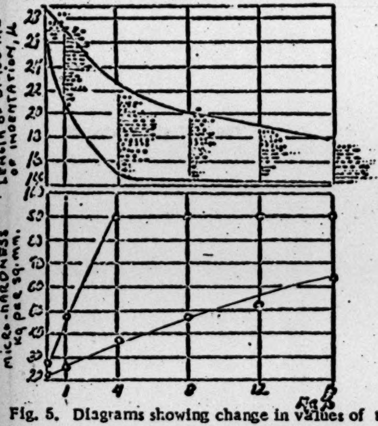


Fig. 5. Diagrams showing change in values of the diagonals of indentations and of micro-hardness in different zones of grains of solid solution Al-Mg.

Fig. 7 (see plate p. 254-a) is a photomicrograph of a section of an alloy containing 8% of Mg. It is evident that the deepest indentations (minimum hardness) are toward the center of the grain, and the shallowest ones are at the periphery.

The hardness diagram for antimony-bismuth alloys is given by Fig. 6. These elements form a continuous series of solid solutions. In solidifying, the central part of a grain forms a solid solution, the composition of which varies continuously from alloy to alloy, from pure bismuth to pure antimony. The composition of the peripheral zones of the grains of all alloys will in the limiting case (with total suppression of diffusion in the solid phase during crystallization) be that of pure bismuth. For this reason, the upper curve of the hardness diagram (lower part of Fig. 6) for rapidly cooled alloys should resemble the hardness curve for a continuous series of solid solutions, i.e., it should be a curve with the convexity directed upwards, as was shown by Kurnakov. The lower curve of the hardness diagram should be in the limiting case a straight line, since it should for all alloys correspond with the hardness of pure bismuth.

The experimental curve is a straight line, gently sloping upwards to 50% of Sb, above which it rises more abruptly. As in the case of Al — Mg alloys, this is evidently due to the circumstance that at the given rate of cooling diffusion in the solid phase was not totally abolished. The photomicrograph of the 50% Sb alloy (Fig. 8) shows zones consisting preponderatingly of bismuth as black, and of antimony as light, areas; the deepest impressions (smallest hardnesses) are to be found in the black parts, and the most shallow ones in the light parts.

CONCLUSIONS

1. Intra-crystalline liquation of alloys of aluminum and magnesium and of bismuth and antimony has been

studied by the micro-hardness method.

2. The hardness of the alloys varies in accordance with the theoretical considerations previously advanced.

LITERATURE CITED

[1] D. A. Petrov, J. Phys. Chem., 21, No. 12 (1947).

[2] A. A. Bochvar and O.S. Zhadaeva, Bull. Acad. Sci. US.S.R., Div. Tech. Sci., 10-11 (1945).

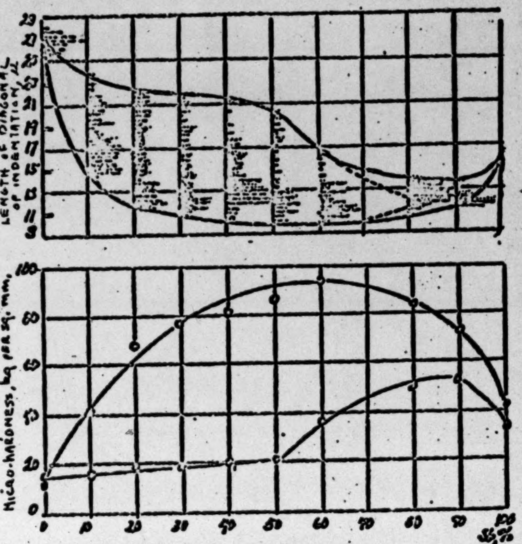


Fig. 6. Diagrams showing change in values of the diagonals of indentations and of micro-hardness in different zones of grains of solid solution Sb-Bi.

Received July 16, 1951

N.S. Kurnakov Institute of
General and Inorganic Chemistry,
Academy of Sciences, USSR

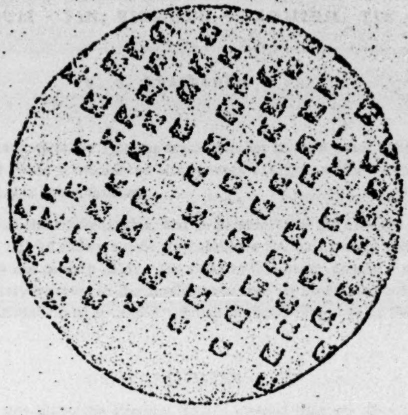


Fig. 7. Photomicrograph of indentations made on ground cross-sections of an alloy of Al with 8% of Mg. Cooled in air. (X 300).

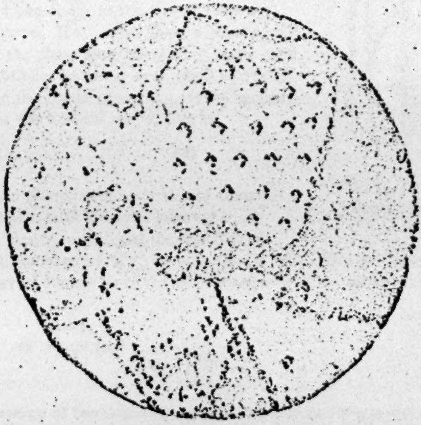


Fig. 8. Photomicrograph of indentations made on ground cross-sections of an alloy of Bi with 50% Sb. Cooled in an oven. Etched with 50% HNO_3. (X 300).

BLANK
PAGE

THERMODYNAMIC STUDY OF THE SYSTEMS CADMIUM - ZINC, CADMIUM - LEAD, CADMIUM - TIN, BISMUTH - CADMIUM, TIN - ZINC, and LEAD - TIN

V. S. Lyashenko

The phase diagrams of binary metallic systems are at present in most cases sufficiently well known. We know that the formation of one or another phase is associated with energy changes, of the dimensions of which, and of the rules governing which, we in most cases know nothing.

The application of chemical thermodynamics, and in particular of the concept of thermodynamic activity, to the phase diagram enables us, as will be shown below, to calculate the free energy and the heat of formation of any particular phase separating from the molten alloy. We shall in this paper present a method for the calculation of the activity of components of binary systems in the liquid state, and we illustrate its application to the calculation of the free energy and the heat of formation of α- and β- phases in phase diagrams of the type corresponding with limited solubility in the solid state.

GENERAL PRINCIPLES

If a pure component separates along the liquidus line of a phase diagram then the free energy of its separation (solidification) and its activity, relative to the component in the liquid state, taken as the standard state, are given by the following expression [1]:

$$\Delta F = -RT \ln a_s \qquad (1)$$

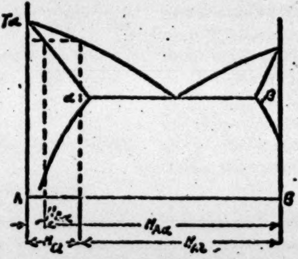


Fig. 1. Phase diagram for the case of limited solubility in the solid state.

Since the pure component separating out is in equilibrium with the same component in the liquid state, the activity a_s of the solid component will be equal to its activity in the liquid phase, a_l, at the temperature and composition given by the liquidus curve. If the solid phase separating out towards the side of component A of the phase diagram (Fig. 1) is the solid solution α, which may for low solubilities be taken as an ideal solution, then the activity of component A in the liquid phase, a_{Al}, at the temperature and composition determined by the liquidus curve, will be

$$a_{Al} = a_{As} N_{A\alpha}. \qquad (2)$$

At temperature T the liquid phase, with activities of components a_{Al} and a_{Bl}, will be in equilibrium with the solid solution α, of composition $N_{A\alpha}$ and $N_{B\alpha}$ g-mol. Hence, expressing the reaction of formation of one gram-atom of solid solution by $N_{A\alpha} \cdot A + N_{B\alpha} B = \alpha$ and taking the activity of the solid solution as being equal to unity, the free energy of formation of the solid solution α of the given composition from the liquid phase will be given by

$$\Delta F = -RT \ln \frac{1}{a_{Al}^{N_{A\alpha}} \cdot a_{Bl}^{N_{B\alpha}}} \qquad (3)$$

Having derived the free energy of formation of α-phase at different temperatures and compositions, in accordance with the given phase diagram, and knowing the relation

$$\frac{d\Delta F/T}{d\,1/T} = \Delta H \qquad (4)$$

derived from the Gibbs-Helmholtz equation, we construct a curve, with ordinates $\Delta F/T$ and abscissae $1/T$. The tangent of the angle between the tangent at the given point of the curve relating temperature with composition of the α-phase and the horizontal axis gives the value of the heat of formation of solid solution from the liquid phase.

It is necessary, in order to derive the heat of formation of solid solution from its solid components, to add to the heat of formation of solid solution from the liquid phase the heat of fusion of components A and B and to subtract or add the heat of mixing of the liquid components A and B, in proportions corresponding with those present in the α-phase. The heat of mixing should be added when the reaction of mixing the liquid components is endothermic, and subtracted when it is exothermic.

This method for calculating the activity of the components of liquid alloys, and of the free energy and heat of formation of solid solutions in systems with limited solid solubility, will be applied below to a number of systems. The system cadmium-zinc will be discussed most fully, only the experimental results and the curves being given for the other systems. We shall in this paper apply thermodynamic representation, i.e., if a process proceeds with evolution of heat, this will be designated by a minus sign. All calculations are related to a gram-atom of alloy.

THE SYSTEM CADMIUM-ZINC

Activity of cadmium and zinc in the system cadmium-zinc.

The phase diagram of the system cadmium-zinc has been exhaustively studied by a number of authors, and the relevant data, taken from Hansen's compilation [2] are given in Table 1. These data serve for supplying the necessary critical points for the thermodynamic treatment of the phase diagram.

TABLE 1

N_{Cd_l}	0.9	0.8	0.734 eutectic	0.7	0.6	0.5	0.4	0.3	0.2	0.1
T_1	569	547	539	547	566	581	596	608	626	651
N_{Cd_α}	0.975	0.966	0.950	–	–	–	–	–	–	–
N_{Zn_β}	–	–	0.987	0.987	0.986	0.985	0.984	0.984	0.984	0.987

In Table 1 T is the temperature at which separation of α- or β-phase begins, at a molar concentration of cadmium in the liquid phase of N_{Cd_l}; N_{Cd_α} and N_{Zn_β} are the molar concentrations of cadmium and zinc, respectively, in the solid solutions α and β, in equilibrium with the liquid phases at the corresponding temperature.

The specific heat of cadmium and zinc in the solid and liquid states, and their latent heats of fusion, are taken from the book "Thermal constants of inorganic substances" [3], and the equations relating latent heat of fusion to temperature are hence derived:

For cadmium $\Delta H = 904 + 1.67 \cdot T - 1.233 \cdot 10^{-3} \cdot T^2$ (5)
For zinc $\Delta H = 491 + 2.34 \cdot T - 1.075 \cdot 10^{-3} \cdot T^2$ (6)

After substituting for ΔH in the Gibbs-Helmholtz equation, and integrating, we obtain the following expressions connecting free energy of fusion (solidification) with temperature:

For cadmium $\Delta F = 904 - 1.67 \cdot T \ln T + 1.233 \cdot 10^{-3} \cdot T^2 + 8.415.$ (7)
For zinc $\Delta F = 491 - 2.34 \cdot T \ln T + 1.075 \cdot 10^{-3} \cdot T^2 + 13.856.$ (8)

where 8.415 and 13.856 are integration constants, following from the condition that at the melting point $\Delta F = 0$.

The activites of cadmium and zinc in the liquid phase are given in Table 2 (figures not in parentheses); the values are derived from equations (1), (7) and (8) for temperatures and compositions corresponding with those of the liquidus curve, up to, and including the eutectic point.

The calculation of the activities for any other temperature is performed by means of the equation

$$\frac{d \ln a}{dT} = -\frac{\overline{L}}{RT^2}.$$

This equation is integrated between the limits T_1 to T_2, assuming $\overline{L}$ to be independent of temperature, and after substituting the values of constants we obtain:

$$\ln a_{T_2} = -\frac{\bar{L}}{4.575}\left(\frac{T_2 - T_1}{T_2 \cdot T_1}\right) + \ln a_{T_1} \qquad (9)$$

where $\bar{L}$ is the partial heat of mixing derived by a graphical method [1] from Kawakami's data for heats of mixing [4], and presented in Table 3.

Activities calculated by us for cadmium and zinc for temperatures of up to 700°K are presented in Table 4 (not those marked with an asterisk). The same Table also gives other data, the significance of which requires no explanation; these data will be required by us for the calculation of activities of cadmium and zinc not available to us. We know the activities of cadmium and zinc only up to the eutectic composition, from each side of the phase diagram, i.e., corresponding with the liquidus curves of the diagram.

TABLE 2

N_{Cd_1}	0.9	0.8	0.734	0.7	0.6	0.5	0.4	0.3	0.2	0.1
T_1	569	547	539	547	566	581	596	608	626	651
a_{Cd}	0.919	0.865	0.838	(0.824)	(0.781)	(0.749)	(0.699)	(0.648)	(0.562)	(0.374)
a_{Zn}	(0.460)	(0.624)	0.717	0.732	0.769	0.792	0.816	0.840	0.867	0.919

TABLE 3

N_{Zn}	0.00	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
$\bar{L}_{Zn}\ \frac{\text{cal}}{\text{g-atom}}$	1300	1232	1175	1025	925	500	246	185	138	46	0
$\bar{L}_{Cd}\ \frac{\text{cal}}{\text{g-atom}}$	0.0	0.0	16	64	117	486	762	875	1026	1156	2100

The remaining activities of zinc are calculated in the following way. A graph (Fig.2) is constructed, in which the ordinates are the ratio N_{Zn}/N_{Cd}, and the abscissas are log a_{Zn}/N_{Zn}. The curve ends with the activity and the molar ratio for zinc at the eutectic composition; we continue it, along the broken line, to $N_{Cd}/N_{Zn} = 0$. From the Gibbs-Duhem equation

$$\int_0^{\log \frac{a_{Cd}}{N_{Cd}}} d \log \frac{a_{Cd}}{N_{Cd}} = \int_0^{\frac{N_{Zn}}{N_{Cd}}} \frac{N_{Zn}}{N_{Cd}} \cdot d \log \frac{a_{Zn}}{N_{Zn}}$$

by graphical integration, and with the known activities of cadmium at $N_{Cd} = 0.9$, 0.8, and 0.736, we obtain the following

$$\log \frac{a_{Cd}}{N_{Cd} = 0.8} = \log \frac{a_{Cd}}{N_{Cd} = 0.9} + \frac{bb' + cc'}{2}\ bc,$$

whence we derive $bc = \frac{(0.0328 - 0.0107) \cdot 2}{0.111 - 0.250} = 0.1203.$

And further,

$$\log \frac{a_{Cd}}{N_{Cd} = 0.734} = \log \frac{a_{Cd}}{N_{Cd} = 0.8} + \frac{aa' + bb'}{2}\ ab,$$

whence $ab = \frac{(0.0545 - 0.0328) \cdot 2}{0.250 + 0.365} = 0.0706.$

We see from Fig.2 that:

TABLE 4

N_{Zn}	$\frac{N_{Zn}}{N_{Cd}}$	a_{Zn}	$\frac{a_{Zn}}{N_{Zn}}$	$\log\frac{a_{Zn}}{N_{Zn}}$	a_{Cd}	$\frac{a_{Cd}}{N_{Cd}}$	$\log\frac{a_{Cd}}{N_{Cd}}$
0.9	9.00	0.916	1.018	0.0077	0.344*	3.436	0.5361
0.8	4.00	0.857	1.072	0.0302	0.515*	2.576	0.4114
0.7	2.33	0.823	1.177	0.0702	0.589*	1.965	0.2933
0.6	1.50	0.792	1.321	0.1206	0.635*	1.589	0.2011
0.5	1.00	0.736	1.473	0.1681	0.697*	1.394	0.1441
0.4	0.667	0.657	1.643	0.2156	0.766*	1.278	0.1061
0.3	0.428	0.590	1.968	0.2938	0.813*	1.163	0.0653
0.266	0.365	0.557	2.092	0.3212	0.832	1.134	0.0545
0.2	0.250	0.493*	2.466	0.3918	0.863	1.079	0.0328
0.1	0.111	0.325*	3.250	0.5121	0.922	1.025	0.0107

$$\log\frac{a_{Zn}}{N_{Zn}=0.2} = \log\frac{a_{Zn}}{N_{Zn}=0.266} + ab,$$

whence, after substitution of the appropriate values, we obtain

$$\frac{a_{Zn}}{N_{Zn}=0.2} = 2.466;\ a_{Zn} = 0.493.$$

Similarly,

$$\log\frac{a_{Zn}}{N_{Zn}=0.1} = \log\frac{a_{Zn}}{N_{Zn}=0.2} + bc,$$

whence

$$\frac{a_{Zn}}{N_{Zn}=0.1} = 3.25;\ a_{Zn} = 0.325.$$

The missing activities of cadmium are found similarly, but in this case the ordinates of the curve are N_{Cd}/N_{Zn}, and the abscissas $\log a_{Cd}/N_{Cd}$. The activities of cadmium and zinc calculated in this way are marked with an asterisk in Table 4.

The relation between the activities of cadmium and zinc at 700°K and their relative molar concentrations is shown in Fig.3, which also shows activities for cadmium and zinc according to Taylor's data [5] for 708°K, derived from e.m.f. measurements, as well as Burmeister and Jellinek's results [6] for 955°K, derived from vapor pressure measurements. It is evident that our results are in good agreement with those of Taylor, but that Burmeister and Jellinek's results are in general lower than ours; this is ascribable to the higher temperature to which their results refer, since it is known that positive deviations of activity diminish with rising temperature.

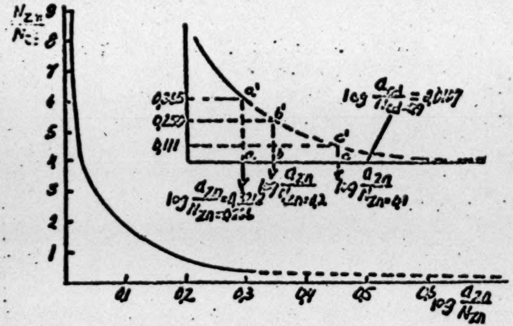


Fig.2. Determination of missing activities of zinc in the system cadmium-zinc.

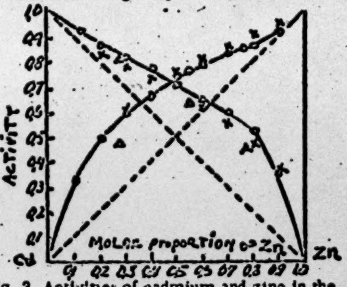


Fig. 3. Activities of cadmium and zinc in the system cadmium-zinc: o – our values, for 700°K; x – Taylor's values for 708°K; Δ – Jellinek's values, for 955°K.

Free energy and heat of formation of α- and β-phases in the system cadmium-zinc

The activities of zinc have first to be calculated before we can calculate the free energy of formation of the α-phase, from equation (3), at the temperature and composition corresponding to the liquidus curve for separation of α-phase, according to equation (9). We already have the corresponding values for cadmium, given in Table 2. Similar calculations are performed for derivation of the free energy of formation of the β-phase, in accordance with the temperature and composition determined by the liquidus curve for separation of β-phase. The results so calculated for the activity of zinc are given in Table 2 (in parentheses).

The calculated free energies, and the graphically derived heats of formation (Fig.4) of the α- and β-phases from liquid mixtures of the system cadmium-zinc, are given in Table 5, for various temperatures and compositions.

The curve relating $-\Delta F/T$ to $1/T$ is practically rectilinear for the α- and β-phases of the system cadmium-zinc, which suggests that the heat of formation of these phases from the liquid components is practically independent of temperature and composition, and amounts for the α-phase to −1580 cal per g-atom, and for the β-phase to −1430 cal per g-atom. This linear relationship between $-\Delta F/T$ and $1/T$ is not, as will appear below, found for solid solutions of variable composition separating from certain other systems.

From the values obtained for the heats of formation of the α- and β-phases from liquid mixtures, the latent heats of fusion of cadmium and zinc calculated from equations (5)' and (7), and the heats of mixing of the liquid components, we derive the heat of formation of α-phase at the eutectic temperature from the solid components; the value found is −135 cal per g-atom (exothermic reaction), while for the β-phase it is 13 cal per g-atom, i.e., it is practically zero. Weibke and Kubaschewsky [7] found that the heat of formation of solid alloys of this system from their solid components was practically equal to zero, as might be expected from the negligible mutual solubility of cadmium and zinc at 100° [2], while the formation of eutectic mixtures from their pure components should not be associated with any perceptible thermal effect. The free energy of formation of α-phase from the solid components, calculated similarly, amounts to −50 cal per g-atom, and of the β-phase to −14 cal per g-atom (neglecting, as being very small under the given conditions, change in free energy due to mixing).

TABLE 5

α-phase					β-phase				
N_{Cd_l}	N_{Cd_α}	T_l	$-\Delta F \frac{cal}{g\text{-atom}}$	$-\Delta H \frac{cal}{g\text{-atom}}$	N_{Zn_l}	N_{Zn_β}	T_l	$-\Delta F \frac{cal}{g\text{-atom}}$	$-\Delta H \frac{cal}{g\text{-atom}}$
0.9	0.975	569	115	1580	.0.9	0.987	651	126	1430
0.8	0.966	547	170	1580	0.8	0.984	626	186	1430
0.734	0.950	539	196	1580	0.7	0.984	608	217	1430
					0.6	0.984	596	244	1430
					0.5	0.985	581	270	1430
					0.4	0.986	566	295	1430
					0.3	0.987	547	337	1430
					0.266	0.987	539	354	1430

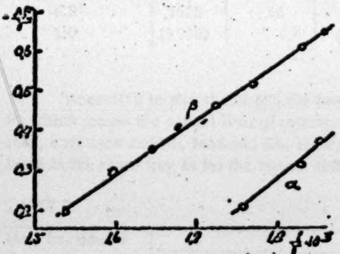


Fig.4. Heats of formation of α- and β-phases from liquid alloys of the system cadmium-zinc

Cadmium-Lead, Cadmium-Tin, Lead-Tin, Bismuth-Cadmium, and Tin-Zinc Systems

Activities of cadmium and lead, cadmium and tin, lead and tin, bismuth and cadmium, and tin and zinc in the appropriate liquid systems.

The critical points of the phase diagrams were taken from the data of a number of authors, as compiled by Hansen [2]. The solubility of lead in cadmium is taken as negligible. That of cadmium in lead at the eutectic temperature is taken from Tamman and Ruedger [2] as being equal to 0.0715 mol parts. The solubility of cadmium in tin and of tin in cadmium are taken from Le Blanc [2] as being 0.0787 and 0.0313 mol parts, respectively, at the eutectic temperature. The solubility of lead in tin and of tin in lead are taken from the figures of a number of authors quoted by Hansen [2] as being 0.015 and 0.297 mol parts, respectively, at the eutectic temperature. The mutual solubilities of the systems bismuth-cadmium and tin-zinc are taken as being negligible in the solid state.

The latent heat and the free energies of fusion of the components of the systems under consideration have been calculated for various temperatures from the thermal data given in the literature [3], using the following equations:

For lead $\Delta H = 970 + 1.03\cdot T - 1.01\cdot 10^{-3}\cdot T^2;$ (10)

$\Delta F = 970 - 1.03\cdot T \ln T + 1.01\cdot 10^{-3}\cdot T^2 + 4.370\cdot T.$ (11)

For tin $\Delta H = 1550 + 1.55\cdot T - 2.40\cdot 10^{-3}\cdot T^2;$ (12)

$\Delta F = 1550 - 1.55\cdot T \ln T + 2.40\cdot 10^{-3} T^2 + 5.347\cdot T.$ (13)

For bismuth $\Delta H = 1809 + 2.11\cdot T - 1.22\cdot 10^{-3}\cdot T^2;$ (14)

$\Delta F = 1809 - 2.11\cdot T \ln T + 1.22\cdot 10^{-3} T^2 + 9.311\cdot T.$ (15)

Equations (5), (7), (6), and (8) were used for cadmium and zinc. The partial heats of mixing, derived graphically from the heats of mixing [4] of the components of the systems, are given in Table 6.

TABLE 6

Mol. fraction of first component	System							
	Cadmium-lead, at 633°K		Cadmium-tin, at 623°K		Lead-tin, at 623°K		Tin-zinc, at 723°K	
	$\bar{L}_{Cd}$ cal/g-atom	$\bar{L}_{Pb}$ cal/g-atom	$\bar{L}_{Cd}$ cal/g-atom	$\bar{L}_{Sn}$ cal/g-atom	$\bar{L}_{Pb}$ cal/g-atom	$\bar{L}_{Sn}$ cal/g-atom	$\bar{L}_{Sn}$ cal/g-atom	$\bar{L}_{Zn}$ cal/g-atom
0.0	0.0	(2140)	0.0	(1300)	0.0	(1065)	0.0	(2800)
0.1	25	1867	15	1085	17	905	-38	2400
0.2	85	1537	45	915	44	768	115	1940
0.3	196	1212	86	790	73	668	222	1655
0.4	510	620	182	615	135	560	337	1445
0.5	702	373	318	455	434	198	1085	615
0.6	674	225	595	225	576	78	1495	237
0.7	1055	135	860	108	660	30	1750	110
0.8	1305	55	920	67	695	20	1955	35
0.9	1515	16	1215	20	742	12	2135	15
1.0	(1760)	0.0	(1600)	0.0	(810)	0.0	(2300)	0.0

According to Kawakami [4], the heat of mixing of liquid bismuth and cadmium at 350° is practically zero, for which reason the partial heat of mixing of these metals is also taken to be zero. The activities of cadmium and lead, cadmium and tin, lead and tin, bismuth and cadmium, and tin and zinc in the corresponding systems, calculated in the same way as for the system cadmium-zinc, are given in Table 7.

TABLE 7

Mol. fraction of first component	System									
	Cadmium-lead at 705°K		Cadmium-tin at 704°K		Lead-tin at 623°K		Bismuth-cadmium		Tin-zinc at 723°K	
	a_{Cd}	a_{Pb}	a_{Cd}	a_{Sn}	a_{Pb}	a_{Sn}	a_{Bi}	a_{Cd}	a_{Sn}	a_{Zn}
0.9	0 932	0.390	0.915	0.204	0.905	0.227	0.892	0.127	0.911	0.1975
0.8	0.898	0.498	0.844	0.321	0.836	0.368	0.798	0.241	0.819	0.368
0.7	0.870	0.551	0.798	0.405	0.781	0.455	0.702	0.357	0.731	0.519
0.6	0.807	0.636	0.718	0.492	0.715	0.536	0.616	0.455	0.651	0.642
0.5	0.765	0.681	0.641	0.564	0.626	0.633	0.524	0.554	0.549	0.792
0.4	0.712	0.725	0.549	0.647	0.543	0.712	0.428	0.654	0.493	0.862
0.3	0.654	0.761	0.442	0.736	0.453	0.786	0.329	0.751	0.459	0.894
0.2	0.514	0.822	0.318	0.820	0.360	0.848	0.252	0.820	0.407	0.928
0.1	0.287	0.907	0.182	0.900	0.239	0.907	0.141	0.904	0.345	0.949

Since the partial heat of mixing is, according to Kawakami [4] practically zero for bismuth and cadmium, the activities of bismuth and cadmium in the system bismuth-cadmium, given in Table 7, are not re-calculated for any other temperature. The composition of the eutectic given by Hansen for this system is 40% by weight of cadmium, but the activities calculated on this basis do not give smooth curves for bismuth and cadmium. For this reason, we have taken the value of 39.1% by weight of cadmium as the composition of the eutectic, this figure being the mean of eight values derived by various authors.

Figs. 5, 6, 7, 8, and 9 give the curves relating calculated activities to mol concentration of the components of the systems. It is evident from Figs. 5, 6 and 9 that the calculated activities are in very good agreement with those obtained experimentally by Taylor [5] from e.m.f. measurements.

Jellinek's data [8] for the system tin-zinc at 973°K are somewhat below our calculated ones, as was to be expected, since positive deviations of activity from Raoult's law should diminish with rising temperature. Agreement is not so good, however, for the system bismuth-cadmium (Fig.8). We see that the calculated activities of cadmium exhibit positive deviations from Raoult's law over the whole range of concentrations; for bismuth positive deviations are found only in systems with a mol fraction of Bi of 0 to 0.6. Yet, according to Taylor's experimental results [5], alloys with a mol fraction of Cd of 0 to 0.6 should exhibit negative deviations, and the same applies to activities of bismuth in alloys containing 0 to 50 atomic-% of bismuth.

This difference between calculated and experimental values of activities cannot be ascribed to inaccurate determination of the liquidus curve, since this phase diagram has been subjected to adequate study by a number of authors [2]. Nor can it be due to inaccuracies in the published thermal data for bismuth and cadmium, since these are known to be sufficiently accurate [3], or to an error in the method adopted for the calculation, since our method is thermodynamically sound, and its validity is confirmed by the curves for a number of systems, given above.

Bearing in mind that, for the system bismuth-cadmium, the liquidus curve is situated somewhat above that which would follow from the theoretical position based on Schroeder's equation [9], it might be said that the system does not follow Raoult's law, since attractive forces between like atoms prevail over those between unlike atoms. The mixing of the liqud components should hence be associated with absorption of heat.

The negative deviations of activity of bismuth and cadmium shown by Taylor's results would indicate that attractive forces between unlike atoms should prevail, that mixing of the liquid components should be associated with a slight evolution of heat, and that the liquidus curves should lie below those calculated from Schroeder's equation; this is not in fact the case. We may therefore assume that the activities of bismuth and cadmium calculated by us for this sytem are closer to the real values.

The calculated activities of lead and tin in the system lead-tin cannot be compared with experimental values, since it is not possible to determine these values by any known method, owing to the small differences between the electrode potentials and the vapor pressure of tin and lead. Thus our thermodynamic method of calculating the activities of the components of such systems is the only possible one.

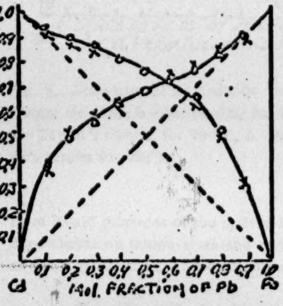


Fig. 5. Activities of cadmium and lead in the system cadmium-lead: o - our values, for 705°K, x - Taylor's values, for 705° K.

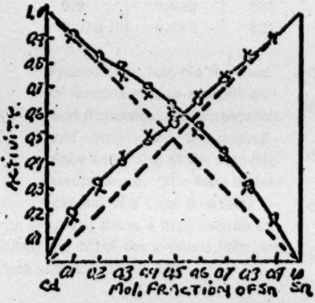


Fig. 6. Activities of cadmium and tin in the system cadmium-tin: o - our values, for 704°K, x - Taylor's values, for 704°K.

Free Energy and Heat of Formation of Solid Solutions in the Systems Cadmium-Lead, Cadmium-Tin, and Lead-Tin

The free energy $\Delta \underline{F}$ and the heat of formation $\Delta \underline{H}$ of solid solutions from liquid mixtures in the given systems, and the heat of formation of solid solutions from the solid components, $\Delta \underline{Q}$, at the eutectic temperature, were calculated in the same way as for the system cadmium-zinc. The calculations were made only for the β-phase of the system cadmium-lead, since we take the solubility of lead in cadmium as being negligible. The results of these calculations are given in Table 8 and in Fig. 10, for the system cadmium-tin in Table 9 and Fig. 11, and for the system lead-tin in Table 10 and Fig. 12.

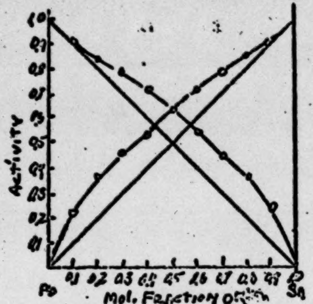


Fig. 7. Activities of lead and tin in the system lead-tin: o - our values, for 623°K

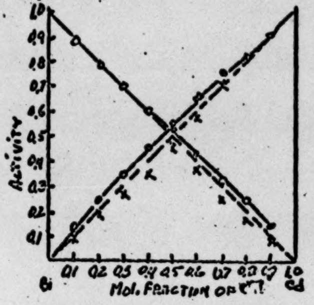


Fig. 8. Activities of bismuth and cadmium in the system bismuth-cadmium: o - our results, x - Taylor's results, for 704°K.

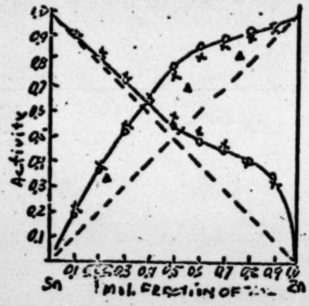


Fig. 9. Activities of tin and zinc in the system tin-zinc: o - our results, for 723°K x - Taylor's results, for 704°K, Δ - Jellinek's results for 973°K.

As may be seen from Figs. 10 and 11, the heat of formation of the β-phase of the systems cadmium-lead and cadmium-tin is practically independent of temperature and composition, while for the α-phase of the system cadmium-tin the heat of formation is to a small extent dependent on temperature and composition, this dependence vanishing at the eutectic temperature. The heat of formation of α- and β-phases from liquid mixtures of the system lead-tin (Fig. 12) shows a high degree of dependence on temperature and composition; the $\Delta \underline{H}$ of the α-phase falls, and of the β-phase rises, with diminution in temperature (Table 10).

TABLE 8

$N_{Pb_{\underline{l}}}$	$N_{Pb_{\beta}}$	$T_{\underline{l}}$	−ΔF cal per g-atom	−ΔH cal per g-atom	−ΔQ cal per g-atom
0.9	0.970	564	136	1464	295
0.8	0.946	535	205	1464	295
0.719	0.929	521	237	1464	295

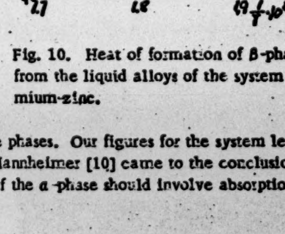


Fig. 10. Heat of formation of β-phase from the liquid alloys of the system cadmium-zinc.

The values calculated by us for the heats of formation of solid solutions from the solid components for the systems cadmium-lead and cadmium-tin cannot be compared with experimentally obtained data, since the only available published figures [Magnus and Mannheimer, 10] refer to alloys containing 50 atomic-% of each component, and not to the separate phases. Our figures for the system lead-tin are in agreement with published experimental data. Thus, Magnus and Mannheimer [10] came to the conclusion, on the basis of Taylor's and of their own experimental data, that formation of the α-phase should involve absorption of 400 cal. per g-atom, and of the β-phase evolution of 500 cal. per g-atom.

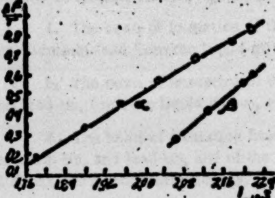


Fig. 11. Heat of formation of α- and β-phases from the liquid alloys of the system cadmium-tin.

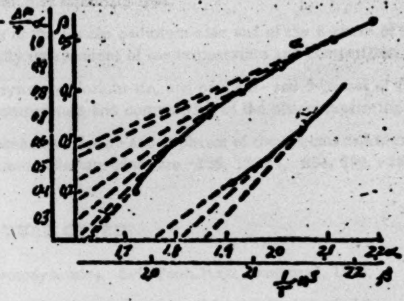


Fig. 12. Heat of formation of α- and β-phases from liquid alloys of the system lead-tin.

TABLE 9

α-phase						β-phase					
N_{Cd_1}	N_{Cd_α}	T_1	−ΔF cal per g-atom	−ΔH cal per g-atom	−ΔQ cal. per g-atom	N_{Sn_1}	N_{Sn_β}	T_1	−ΔF cal per g-atom	−ΔH cal per g-atom	−ΔQ cal per g-atom
0.9	0.993	561	105	1770	–	0.9	0.970	485	131	2100	–
0.8	0.987	533	179	1505	–	0.8	0.950	470	193	2100	–
0.7	0.982	513	233	1464	–	0.7	0.928	455	253	2100	–
0.6	0.978	493	276	1392	–	0.665	0.921	450	269	2100	294
0.5	0.974	475	319	1390	–						
0.4	0.971	459	338	1390	–						
0.261	0.969	450	377	1390	−47						

TABLE 10

α-phase						β-phase					
N_{Pb_1}	N_{Pb_α}	T_1	−ΔF cal per g-atom	−ΔH cal per g-atom	−ΔQ cal per g-atom	N_{Sn_1}	N_{Sn_β}	T_1	−ΔF cal per g-atom	−ΔH cal per g-atom	−ΔQ cal per g-atom
0.9	0.942	584	204	2940	–	0.9	0.990	481	104	1350	–
0.8	0.902	574	285	2360	–	0.8	0.987	465	153	1770	–
0.7	0.863	552	334	1830	–	0.739	0.985	456	187	2100	392
0.6	0.824	536	381	1540	–						
0.5	0.793	517	412	1310	–						
0.4	0.758	497	446	1150	–						
0.3	0.719	470	476	910	–						
0.261	0.702	456	488	890	−694						

SUMMARY

1. A thermodynamic method is presented, for calculating activities of components of binary systems in the liquid state, which give eutectics on solidification. Activities calculated for the components of the systems cadmium-zinc, cadmium-tin, cadmium-lead, and tin-zinc are in full agreement with published values.

2. Activities have been calculated for lead and tin in the system lead-tin, for which these values have not yet been determined experimentally.

3. A thermodynamic method is given, for calculation of the heat and free energy of formation of solid

solutions in systems with a phase diagram of the limited mutual solubility type.

4. The heats of formation of the α- and β-phases of the system cadmium-zinc and of the β-phase of the system cadmium-lead from the liquid mixtures are practically independent of the temperature and composition.

5. The heats of formation of the α-phase of the system cadmium-tin, and of the α- and β-phases of the system lead-tin, from the liquid phases, vary according to temperature and composition of the phases separating out.

6. The heats of formation from their solid components of the α- and β-phases of the systems cadmium-zinc, cadmium-tin, and lead-tin, and of the β-phase of the system cadmium-lead, are −135, 13, 47, −294, 694, −392, and −295 cal. per g-atom, respectively.

LITERATURE CITED

[1] D. N Lewis and M Randall. Chemical Thermodynamics. Sci.-Tech. Press, Leningrad, 1936.

[2] M. Hansen. Structures of Binary Alloys. Sci.-Tech. Press, Moscow-Leningrad, 1941.

[3] E. V. Britske, A. F. Kapustinsky, B.K. Veselovsky, L. M. Shamovsky, L.G. Chentsova, and B. I. Anvaer. Thermal Constants of Inorganic Substances. Published by the Academy of Sciences, U.S.S R., Moscow-Leningrad, 1949.

[4] M. Kawakami, Z. anorg. allg. Chem. 167, 345 (1927).

[5] N.W. Taylor, J. Am. Chem. Soc., 45, 2865 (1923).

[6] F. Bernmeister and K. Jellinek, Z. phys. Chem., 165, 121 (1933).

[7] F. Weibke and O. Kubaschewski, Thermochemie, 1943.

[8] K. Jellinek and Hans-Andreas Wannow, Z. Electrochem, 41, 6, 346 (1935).

[9] I. F. Schroeder. Mining Journal, 11, 272 (1890).

[10] A. Magnus and M. Mannheimer, Z. phys. Chem. 121, 267 (1926).

Received August 3, 1951

N.S.Kurnakov Institute of General and Inorganic Chemistry
Academy of Sciences, USSR

KINETICS OF POLYMERIZATION OF COMPOUNDS WITH CONJUGATED DOUBLE BONDS.

POLYMERIZATION OF METHYL ACRYLATE IN ABSENCE OF LIGHT

P. S. Shantarovich

We have shown in our previous communications [1, 2] that, in the polymerization of compounds with conjugated double bonds, the slow reaction, not activated by light, undergoes transition into a rapidly self-accelerating reaction when a certain critical depth of transformation, $\underline{X}_{cr}$, characteristic of each compound, is achieved.

A detailed study of this stage of development of the reaction of polymerization has shown that the phenomenon of self-acceleration of the reaction occurs only when the insoluble form of polymer is produced. The formation and development of this high-molecular insoluble form of polymer, with its new properties, are signalled by the abrupt transition of the reaction into a self-accelerative one.

It was thought to be of interest to elucidate the connection between the observed increase in velocity beyond the critical point $\underline{X}_{cr}$ and the yield of insoluble form of polymer. Fig. 1, Curve 1* shows the kinetics of the reaction of polymerization of methyl acrylate in the absence of light, beyond the point $\underline{X}_{cr}$. The variously designated points of Curve 1 show the closeness of coincidence of four curves obtained with different periods, $\underline{t}_e$, of exposure to light [2]. The rectilinear curve 2 shows how the velocity of polymerization increases with increasing amount of polymer. The results of a study of the composition of the polymers obtained under these same conditions (different $\underline{t}_e$) are given in Table 1, and are shown graphically in Fig. 2, in which the abscissas are total yield of polymer $\underline{X} = \underline{X}_{\alpha} + \underline{X}_{\mu}$, and the ordinates are yield of soluble polymer, $\underline{X}_{\alpha}$, or of insoluble polymer, $\underline{X}_{\mu}$, expressed as moles of transformed monomer. It appears from Table 1 and Fig. 2, that the insoluble form of polymer is practically absent until over 30% of the monomer has been transformed. It appears when the degree of polymerization attains the critical point $\underline{X}_{cr}$, after which the yield of insoluble polymer rises rapidly, and may at any time be expressed by a value directly proportional to the general degree of polymerization. A similar relationship was found for the composition of the products of peroxide-promoted polymerization of chloroprene.

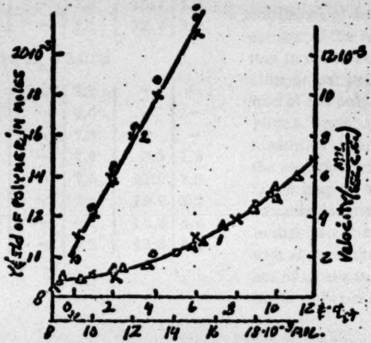


Fig. 1. Polymerization of methyl acrylate in absence of light. 1. Yield of polymer beyond the point $\underline{X}_{cr}$; 2. Dependence of reaction velocity on $\underline{X}_{\mu}$ (x – points obtained experimentally, o – points calculated from the equation); x – $\underline{t}_e$ = 10 min.; o – $\underline{t}_e$ = 15 min.; Δ – $\underline{t}_e$ = 24 min.; ▲ – $\underline{t}_e$ = 32.5 min.
1. Yield of polymer, in moles. 2. Velocity (mol./sec. c.c.)

DISCUSSION OF RESULTS

The equation

$$\frac{dn}{dt} = fn - k_6 X^{-\frac{1}{2}} n^2 ,$$

---

[*] $\underline{t} - \underline{t}_{cr}$ is the time counting from the moment of transition of the reaction, at point $\underline{X}_{cr}$, into a self-accelerative one.

TABLE 1

Relation Between Soluble (α) and Insoluble (μ) Forms of Polymer

$\underline{t}_m$* time in hours	Yield of polymers $X = X_\alpha + X_\mu$						$\underline{t}_m$* time in hours	Yield of polymers $X = X_\alpha + X_\mu$					
	%	$\cdot 10^{-3}$ mol.	α-form		μ-form			%	$\cdot 10^{-3}$ mol.	α-form		μ-form	
			%	$\cdot 10^{-3}$ mol.	%	$\cdot 10^{-3}$ mol.				%	$\cdot 10^{-3}$ mol.	%	$\cdot 10^{-3}$ mol.
t_e = 19 min, X_o = 7.5%							t_e = 19 min, X_o = 14%						
5	10.5	2.97	10.5	2.97	–	–	1	15.7	4.32	15.1	4.32	–	–
30	16.75	4.6	16.75	4.6	–	–	4	17.2	4.7	17.2	4.1	–	–
85	33.0	9.07	16.75	7.07	–	–	10	18.7	5.2	18.7	5.2	–	–
87	33.66	9.25	16.75	7.0	10.2	2.8	30	24.5	6.7	–	6.0	–	–
89	35.46	9.85	–	7.3	–	–	50	32.1	8.8	–	6.4	7.3	2.0
91	40.0	11.0	–	7.1	13.7	3.8	54	36.7	10.1	–	6.5	14.6	4.0
95	48.3	13.2	–	–	20.0	5.5	56	40.4	11.1	–	7.0	14.2	4.4
97	54.49	15.1	–	6.9	28.3	7.8	60	49.1	13.5	–	7.8	16.7	4.6
98	58.2	16.3	–	7.2	34.6	9.5	62	58.0	16.0	–	7.1	32.7	9.0
t_e = 24 min, X_o = 18%							t_e = 33 min, X_o = 24.5%						
1	20.0	5.5	20.0	5.5	–	–	1	26.25	7.2	26.3	7.2	–	–
4	21.1	5.8	21.1	5.9	–	–	3	29.0	7.8	–	7.0	–	–
25	28.3	7.8	–	7.0	–	–	7	30.0	8.3	–	7.3	–	–
35	32.3	8.8	–	7.0	7.3	2.0	16	33.5	9.2	–	7.0	6.5	1.8
40	38.6	10.6	–	7.6	13.7	3.8	20	36.7	10.1	–	7.0	12.0	3.3
42	41.8	11.5	–	7.1	14.0	4.2	22	40.7	11.1	–	7.2	13.7	3.7
44	45.1	12.4	–	7.0	20.0	5.4	24	43.3	11.9	–	6.8	14.2	4.4
46	50.5	13.9	–	7.3	25.6	7.0	27	52.0	14.3	–	6.7	22.6	6.2
50	65.7	–	–	7.0	–	7.8							

applies to the kinetics of the slow reaction of polymerization, proceeding in the dark, but does not apply to the period of rapid increase in velocity. The transition of the reaction at the point $\underline{X}_{cr}$ to one of rapid self-acceleration (Fig. 1) is obviously a manifestation of special conditions of development of the reaction in the three-dimensional structure of the polymer. With a "rigid" three-dimensional structure, the recombination factor may be made vanishingly small, and in that case the change with time in the number of active centers $\underline{N}$ in the polymer lattice is given by the equation

$$\frac{dN}{dt} = \underline{f}N \qquad (1)$$

and the velocity of polymerization, being a function of the amount of insoluble polymer forming, is given by the formula

$$v_\mu = v_{cr} + \underline{f}X_\mu. \qquad (2)$$

where v_{cr} is the velocity of polymerization at the point $\underline{X}_{cr}$, $\underline{f}$ is the branching factor, derivable from the slope of Curve 2 (Fig. 1) as the magnitude of the acceleration of the process in the polymer lattice, $\underline{X}_\mu = \underline{X} - \underline{X}_{\mu cr}$. $\underline{X}_{\mu cr}$ is the amount of insoluble polymer of methyl acrylate formed at the point $\underline{X}_{cr}$.

Equation (2) for the velocity of the reaction in the lattice is valid only in the case when

$$\frac{N}{X_\mu} = \text{const.} \qquad (3)$$

Dividing the equation (1) by $d\underline{X}_\mu/d\underline{t} = \underline{k}_4\underline{N}$ we obtain

$$\frac{dN}{dX_\mu} = \frac{f}{k_4}. \qquad (4)$$

where $\underline{k}_4$ is the specific velocity of growth of the chain, and $\underline{X}_\mu$ is the amount of polymer formed by polymerization within the lattice. This amount is expressed (according to the data of Table 1 and Fig. 2) by the linear relationship:

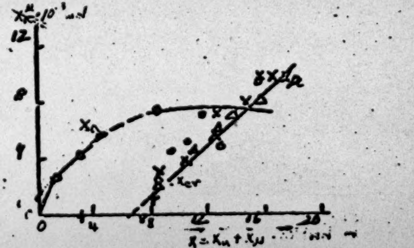


Fig. 2. Relation between soluble (α) and insoluble (μ) forms of polymer, expressed as ratios of overall transformation. x - $\underline{t}_e$ = 10 min; o - $\underline{t}_e$ = 19 min; Δ - $\underline{t}_e$ = 24 min.

---

* $\underline{t}_m$ is time elapsed after extinguishing light.

$$X_{\mu} = \alpha X_{\mu} - X_{\alpha}. \tag{5}$$

and hence

$$\frac{dN}{dX_{\mu}} = a\frac{f}{k_{6}}.$$

Integrating within the limits $\underline{X}_{\mu_0}$ (at the point $\underline{X}_{cr}$) to $\underline{X}_{\mu}$, and from $\underline{N}_0$ (number of active centers in the insoluble polymer formed at the point $\underline{X}_{cr}$) to $\underline{N}_{\mu}$, we obtain

$$N = \alpha\frac{f}{k_{6}}X_{\mu} + [N_0 - \alpha\frac{f}{k_{6}}X_{\mu_0}].$$

It follows from this expression that the experimental dependence of the velocity on $\underline{X}_{\mu}$ is possible only on the condition that

$$N_0 - \alpha\frac{f}{k_{6}}X_{\mu_0} = 0;$$

i.e., that

$$\frac{N}{X_{\mu}} = \frac{N_0}{X_{\mu_0}} = \alpha\frac{f}{k_{6}}; \tag{6}$$

i.e., that the number of active centers in the lattice should grow in proportion to the mass of insoluble polymer.

Since the velocity of polymerization $d\underline{X}_{\mu}/d\underline{t} = \underline{k}_6\underline{N}$, we obtain from equations (5) and (6)

$$\frac{dX}{dt} = \underline{f}X_{\mu}$$

and after integration within the limits X_{μ_0} to X_{μ} and from $\underline{t}_0$ to $\underline{t}$ we obtain

$$X_{\mu} = X_{\mu_0}e^{f(t-t_0)}, \tag{7}$$

where $\underline{t}_0$ is the moment of transition of the reaction to the self-accelerating type, and X_{μ_0} is the amount of insoluble polymer present at that moment. The accuracy of the conclusions arrived at may be checked [formulas (2) and (7)] with the aid of the mean values for velocity and yield of polymer derived from Curves 1 and 2 of Fig. 1, and from the straight line μ of Fig. 2; X_{μ} in formula 2 is understood to be

$$\underline{X}_{\mu} = X_{\mu\,\text{current}} - X_{\mu\,cr}$$

The results of the check are given in Table 2.

TABLE 2

Calculation of Yield of Polymer and of its Rate of Production, Compared with Experimental Values

Time $\underline{t}_{\mu}$, in hours	$X = X_{\alpha} + X_{\mu}$	X_{μ}		v_{μ}	
		Experimental values	Calculated from equation (7)	Experimental values	Calculated from equation (2)
	$\cdot 10^{-2}$	$\cdot 10^{-3}$	$\cdot 10^{-3}$	$\cdot 10^{-6}$	$\cdot 10^{-6}$
0.0	8.9	2.4	2.4	0.018	0.018
2.0	9.2	2.8	2.8	0.030	0.028
4.0	10.0	3.5	3.4	0.040	0.044
6.0	10.9	4.2	4.2	0.060	0.068
8.0	12.0	5.0	4.9	0.079	0.083
10.0	13.1	6.0	5.9	0.100	0.107
12.0	15.0	7.6	7.2	0.130	0.143

$t = 20°$; $X_{cr} = 2.4 \cdot 10^{-3}$ mole; $r_{cr} = 0.018 \cdot 20^{-6}$; $\underline{f} = 2.5 \cdot 10^{-5}$

Good agreement is found between experimental and calculated values of the yield of polymer and of the velocity of polymerization, derived from formulas based on the experimentally justified assumption of the vanishingly small role of recombination of chains in the μ-polymer lattice. Equation (6) applies not only to methyl acrylate, but also to the process of photo-polymerization of chloroprene, methyl methacrylate, and divinyl, and to the peroxide-promoted process of polymerization of chloroprene [3].

The insoluble polymers of methyl acrylate are, similarly to the μ- and ω- polymers of chloroprene, able to catalyze the polymerization of other compounds with conjugated double bonds. The active form of the polymers is obtained only when polymerization is conducted in the absence of a solvent, addition of even quite small amounts of which leads to production of only slightly active, or even of totally inactive, polymers. The condition that $\underline{c}_m = 1$ is obligatory for production of active insoluble polymers. Dilution ($\underline{c}_m < 1$) leads to degeneration of the branching process, which is replaced by simple vinyl polymerization with production of linear polymers.

CONCLUSIONS

1. The velocity of polymerization beyond the point $\underline{X}_{cr}$ is directly proportional to the amount of insoluble polymer formed at any given moment.

2. The expression $\underline{N}/\underline{X}_{\mu}$ = constant is shown to hold for polymerization within the lattice of the polymer (three-dimensional structure).

LITERATURE CITED

[1] P. S. Shantarovich and S. S. Medvedev. J. Phys. Chem., 21, 1163, (1947).

[2] P. S. Shantarovich. Bull. Acad. Sci., U.S.S.R., Div. Chem. Sci. 1, 40 (1952). (See Consultants Bureau English Translation p. 41 ff).

[3] S. Medvedev, O. Koritskaya, and E. Alekseeva. J. Phys. Chem., No. 5-6, 391 (1943).

Received March 30, 1951

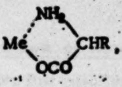
Institute of Chemical Physics
of the Academy of Sciences U.S.S.R.

A NEW CLASS OF COORDINATION COMPOUNDS OF CHROMIUM WITH AMINO-ACIDS

L. M. Volshtein

It is known that α-amino-acids $NH_2CHR \cdot COOH$ can combine with atoms of complex-forming metals in various ways:

a) The metal may be bound to the radicals of the amino-acid, forming a cycle, and occupying two co-ordination places



, in particular, Me⁐Gl* and Me⁐An*; compounds in which such cycles are present are typical coordination complexes.

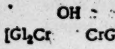
b) The metal (Me) may be bound to the amino-acid molecule in such a way as to occupy one co-ordination place: $Me — NH_2CHR \cdot COOH$, in particular Me—GlH and Me—AnH.

c) The metal may be attached to an open amino-acid radical, occupying one coordination place: $Me — NH_2CHR \cdot COO$, in particular, $Me—\overset{\lrcorner}{Gl}$ and $Me—\overset{\lrcorner}{An}$.

Up till now, the various forms of bonds between amino-acids and metals were realized in practice only for platinum compounds [1-9], such as $[PtGl_2]$, $[Pt(GlH)_4]Cl_2$, $Ba[Pt\overset{\lrcorner}{Gl}_4]$, etc. For copper, cobalt, chromium, and palladium the only known compounds were those containing cyclically bound amino-acid radicals, i.e., the internally complex salts $[CuGl_2]$, $[CoGl_3]$, $[CrGl_3]$, and $[PdGl_2]$ (and the analogous alanine derivatives).

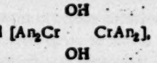
We have prepared about 30 new compounds of chromium with amino-acids (glycerine and alanine); they represent a peculiar and interesting class of co-ordination compound. We present in this paper a general review of these compounds, and give a short description of the results of a physico-chemical study of their aqueous solutions.** Chugaev in 1910 [13] obtained compounds of chromium with glycine, of the composition $CrGl_3$ and $CrGl_2OH$, as well as the compound with alanine $CrAn_3$. Ley [1], repeating Chugaev's work in 1912, obtained another compound with alanine, to which he gave the formula $CrAn_2OH + H_2O$.

We have made a detailed study of these compounds, and have confirmed Chugaev's assumption (using electro-conductivity and other data) that the compounds $[CrGl_3]$ and $[CrAn_3]$ belong to the class of internally complex salts. It has been shown [10] that the compound of the ' ! composition $CrGl_2OH$ is a bi-nuclear diol complex structure



$$[Gl_2Cr\overset{OH}{\underset{OH}{\quad}}CrGl_2]$$

and that the compound to which Ley assigned the formula $CrAn_2OH + H_2O$ is in fact [11] not a hydroxo-aquo-compound, but is a bi-nuclear diol compound



$$[An_2Cr\overset{OH}{\underset{OH}{\quad}}CrAn_2]$$

analogous to the above glycine compound. These bi-nuclear compounds are broken down by prolonged boiling with hydrochloric acid, to give the compounds $[CrGl_2H_2OCl]$ and $[CrAn_2H_2OCl]$, which have been isolated by us.

All four compounds obtained by the above-named authors contain glycine or alanine in the form of cyclically linked radicals, each of which occupies two co-ordination places. Compounds in which chromium is co-ordinated with molecules of glycine (GlH) or alanine (AnH) were first described by us.

---

* We introduce the following conventional symbols: radicals of glycine and alanine forming a cycle are represented by Gl and An; co-ordinated molecules of glycine and alanine, and also free glycine and alanine, are represented by GlH and AnH; open radicals of glycine and alanine, occupying only one co-ordinate place, are represented by $\overset{\lrcorner}{Gl}$ and $\overset{\lrcorner}{An}$.

** A few uncoordinated references relating to some of these compounds have been published earlier [10-12]. For a detailed exposition of the whole research see the author's thesis: "Coordination compounds of tervalent chromium with the simpler amino-acids" (Moscow, Institute of General and Inorganic Chemistry, Academy of Sciences (1950).

Certain French biochemists (Hugounenq, Florence) [14, 15] have suggested formulas for glycine derivatives of chromium, which they believe to contain glycine molecules coordinated to the chromium. We have shown how mistaken was these authors' treatment of the nature of these compounds; they did not even realize that the Gl radicals and the GlH molecules are absolutely different component parts of coordinate compounds. In fact, these authors were dealing with the same compounds which Chugaev had long before prepared.

All the above-mentioned authors conducted their studies of the reactions of tervalent chromium compounds with amino-acids exclusively in alkaline solution. Thus Chugaev, and after him Ley, added excess of glycine (or alanine) to solutions of tervalent chromium salts, which they heated, and then gradually added caustic alkali or ammonia. The reaction was of the following type:

$$CrCl_3 + 3GlH + 3NaOH \longrightarrow [CrGl_3] + 3NaCl + 3H_2O. \qquad (1)$$

The reaction of salts of tervalent chromium with amino-acids in the absence of alkali, and with the solutions remaining acid throughout, has not yet been studied.

EXPERIMENTAL

Preparation of new compounds

We first established that heating solutions of tervalent chromium salts with excess of glycine (or alanine) leads to complex formation, without addition of alkali. The heated solutions change color, and do not give reactions for chromium ion. The final color of the solutions depends on the number of moles of glycine (or alanine) combining with each gram-atom of chromium (this number will hereafter be designated by $\underline{n}$), and on the concentration of the initial solution. If the concentration of the initial chromium chloride solution was about 0.7M, the solutions obtained will have the following colors: $\underline{n} = 3$, green, $\underline{n} = 4$, violet, and $\underline{n} = 5, 6$, or more, red. Addition of caustic alkali or ammonia to the solutions obtained does not precipitate chromium hydroxide from them, either in the cold or after prolonged boiling, if $\underline{n} \geqslant 3$. The solutions may be stored for a long time, and may be evaporated down to fairly small volume, without deposition of any sort of solid phase (at $\underline{n}$ values of 2 to 6; at $\underline{n} > 6$ excess of glycine or alanine deposits).

As the solutions are evaporated down, they become more and more viscous, finally to yield vitreous, noncrystalline, intensely colored solid products, which are readily soluble in water. It is evident that the solutions obtained cannot contain the internally complex salts $[CrGl_3]$ and $[Cr_2Gl_4(OH)_2]$ (or $[CrAn_3]$ and $[Cr_2An_4(OH)_2]$), which are only very slightly soluble in water.

It is possible that earlier workers in this field had noticed that complex formation took place during heating of salts of chromium with glycine or alanine (although no mention of this is made in the literature), but that, since they could see no trace of any precipitates forming, they added alkali, and so shifted the reaction in the direction of formation of internally complex salts. We, however, were interested in the products formed in the solutions in absence of alkali. Our experiments showed that addition of excess of alcohol or acetone to the concentrated solutions (by evaporation down to small volume) leads to separation of a highly viscous product (an "oil"), above which is the colored supernatant aqueous-alcoholic or aqueous acetone solution. The "oil" solidifies after prolonged drying, yielding a non-crystalline product.

We added glycine to known volumes of chromium chloride solutions of known concentration, to give values of $\underline{n}$ of 2, 3, 4, 5, and 6, and the solutions were boiled down to small volumes. Excess of acetone was then added, when the complex salt separated as an "oil", which was separated from the supernatant layer, washed with acetone, and dried to constant weight at 105-110°. Solid products were so obtained, of constant and reproducible composition, corresponding with the formulas: $CrCl_3, H_2O, 2GlH$; $CrCl_3, 3GlH$; $CrCl_3, 4GlH$; $CrCl_3, 5GlH$; $CrCl_3, 6GlH$.

The products obtained with $\underline{n} = 1$ had variable compositions, which were not reproducible.

It may be supposed that the initial reaction taking place when solutions of chromium chloride are heated with glycine is

$$[Cr(H_2O)_6]Cl_3 + nGlH \rightleftarrows [Cr(H_2O)_{6-n}(GlH)_n]Cl_3 + nH_2O. \qquad (2)$$

At the same time, Cl ions enter the inner sphere, leading to an equilibrium such as that illustrated below for the particular case n = 3:

$$[Cr(H_2O)_3(GlH)_3]Cl_3 \rightleftarrows [Cr(GlH)_3Cl_3] + 3H_2O. \qquad (3)$$

Concentration of the solutions by evaporation causes displacement of the equilibria (2) and (3) to the right, and the addition of acetone to the concentrated aqueous solutions causes precipitation of products of the compositions.

$[Cr(GlH)_2H_2OCl_3]$, $[Cr(GlH)_3Cl_3]$, $[Cr(GlH)_4Cl_2]Cl$, $[Cr(GlH)_5Cl]Cl_2$ and $[Cr(GlH)_6]Cl_3$.

Further experiments confirmed the truth of these suppositions as to the nature of the compounds separating, with molecules of amino-acid coordinated with the chromium.

A second method of preparing compounds of this sort was based on the following reasoning. Before we had performed our experiments it might have been supposed that the reaction of GlH with $CrCl_3$ would proceed according to equation (4):

$$CrCl_3 + 3GlH \longrightarrow [CrGl_3] + 3HCl, \qquad (4)$$

The reaction between GlH and chloroplatinite [3] does, in fact, proceed similarly:

$$K_2PtCl_4 + 2GlH \longrightarrow [PtGl_2] + 2HCl + 2KCl.$$

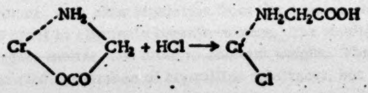
The fact that $[CrGl_3]$ is not obtained from $CrCl_3$ and GlH in absence of alkali led us to the conclusion that glycine cycles coordinated with chromium should be readily opened by hydrochloric acid. For this reason the reaction between GlH and $CrCl_3$ does not proceed according to equation (4), but according to equation (5), which is, for the particular case n = 3, the sum of equations (2) and (3):

$$CrCl_3 + 3GlH \longrightarrow [Cr(GlH)_3Cl_3]. \qquad (5)$$

Experiments in fact showed that $[CrGl_3]$ readily goes into solution when boiled with 0.1M hydrochloric acid. If 3 or more moles of HCl are taken per mole of $[CrGl_3]$, and the solution is evaporated down to small volume, from which addition of acetone causes separation of a green syrup. This is dried to constant weight, to give a product of constant composition $CrCl_3$, 3HCl. The composition and properties of this product are identical with those of the substance obtained by addition of GlH to $CrCl_3$, for the case $\underline{n} = 3$ (the identity of $CrGl_3$, 3HCl with $CrCl_3$, 3GlH is obvious). The opening of the glycine cycles corresponds with the equation:

$$[CrGl_3] + 3HCl \longrightarrow [Cr(GlH)_3Cl_3]. \qquad (6)$$

In this reaction the link between chromium and the carboxyl groups of the cycles is broken, and the radicals Gl become GlH molecules. The Cl anions then enter into the inner sphere, to occupy the places so vacated. This process may be represented schematically as follows:



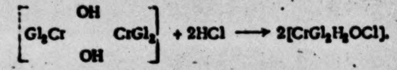
The action of acids (HCl, $H_2C_2O_4$) on the internally complex salts $[CrGl_3]$, $[CrAn_3]$, $[Cr_2Gl_4(OH)_2]$ and $[Cr_2An_4(OH)_2]$ provides us with a second method of preparing compounds in which GlH (AnH) molecules are coordinated with chromium, and we have prepared numerous compounds by this method. When 1 mole of HCl is taken per mole of $[CrGl_3]$ only one of the Gl cycles undergoes opening, and addition of acetone to the solution gives a compound of the composition $[CrGl_2(GlH)Cl]$. With 2 moles of HCl per mole of $[CrGl_3]$ 2 Gl cycles are opened, and the compound $[CrGl(GlH)_2Cl_2]$ is obtained. The following chlorides were obtained similarly from $[CrAn_3]$: $[CrAn_2(AnH)Cl]$, $[CrAn(AnH)_2Cl_2]$, and $[Cr(AnH)_3Cl_3]$.

Successive opening of Gl cycles, with introduction of C_2O_4 or C_2O_4H residues into the inner sphere, is similarly found when oxalic acid is taken instead of hydrochloric acid. With one mole of $H_2C_2O_4$ per mole of $[CrGl_3]$ the reaction proceeds according to the equation:

$$[CrGl_3] + H_2C_2O_4 \longrightarrow [CrGl(GlH)_2C_2O_4]. \qquad (7)$$

Solutions of the compounds $[CrGl(GlH)_2C_2O_4]$, $[Cr(GlH)_3C_2O_4(C_2O_4H)]$ and $[Cr(GlH)_3(C_2O_4H)_3]$ were thus obtained, and the compounds themselves were precipitated by adding excess of alcohol. By acting on $[CrGl_3]$ with hydrochloric and oxalic acids simultaneously the following compounds are obtained: $[Cr(GlH)_3ClC_2O_4]$, $[Cr(GlH)_3Cl(C_2O_4H)_2]$ and $[Cr(GlH)_3Cl_2(C_2O_4H)]$.

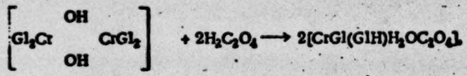
As mentioned above, fission of the complex occurs when one mole of the salt $[Cr_2Gl_4(OH)_2]$ or $[Cr_2An_4(OH)_2]$ is treated with 2 moles of HCl, according to the equation:



$$\left[Gl_2Cr\overset{OH}{\underset{OH}{}}CrGl_2\right] + 2HCl \longrightarrow 2[CrGl_2H_2OCl]. \qquad (8)$$

The product, or its alanine analog $[CrAn_2H_2OCl]$, is precipitated from the concentrated solutions by addition of acetone. The further action of HCl on these monochlorides leads to opening of the Gl cycles and to production of the trichlorides $[Cr(GlH)_2H_2OCl_3]$ or $[Cr(AnH)_2H_2OCl_3]$, and of the dichlorides $[CrGl(GlH)H_2OCl_2]$ and $[CrAn(AnH)H_2OCl_2]$.

Prolonged boiling of a solution of 2 moles of oxalic acid and 1 mole of $[Cr_2Gl_4(OH)_2]$ affords a product of the composition $[CrGl(GlH)H_2OC_2O_4]$ by the following reaction:



$$\left[Gl_2Cr\overset{OH}{\underset{OH}{}}CrGl_2\right] + 2H_2C_2O_4 \longrightarrow 2[CrGl(GlH)H_2OC_2O_4]. \qquad (9)$$

which involves fission of the bi-nuclear complex, with opening of two of the four glycine rings. At the same time part of the original binuclear salt undergoes hydrolysis, with production of chromium hydroxide. The precipitate of $Cr(OH)_3$ is filtered off, and the filtrate is evaporated down to a concentration of about 20% of the main product of the reaction $[CrGl(GlH)H_2OC_2O_4]$, which is then precipitated by addition of alcohol. A compound of the composition $[Cr(GlH)_2H_2OC_2O_4(C_2O_4H)]$ is also obtained by the action of oxalic acid on the bi-nuclear salt, and the compounds $[Cr(GlH)_2H_2OClC_2O_4]$ and $[Cr(GlH)_2H_2OCl(C_2O_4H)_2]$ are given by the action of HCl and $H_2C_2O_4$ together.

Some of the above compounds may be isolated from their aqueous solutions by evaporating these to dryness, on condition that strictly stoichiometric quantities of reagents are taken for their preparation. The vitreous masses obtained are dried to constant weight at 105-115°, to give products of constant and reproducible compositions.

A more general method for their preparation is to precipitate them from their concentrated aqueous solutions by addition of excess of alcohol or acetone. This leads to separation of extremely viscous "oils", which are the actual salts, still retaining small amounts of water. The colored "oils" become even more viscous when washed with alcohol or acetone, and, after separation from the aqueous alcoholic or the aqueous acetone layer, they are dried at 60-70° in order to eliminate organic solvent. The resulting vitreous mass is dried at 105-115°, ground to a powder in an agate mortar, and dried to constant weight. The variously colored powders so obtained in many cases have the outward appearance of crystalline substances, but X-ray and microscopic examination shows the absence of crystalline structure. Their composition was shown by analysis to be constant and reproducible.

It was found that the use of alcohol for separation of chlorine-containing complexes is not permissible, as they remove part of the hydrogen chloride, which remains in the alcoholic layer as ethoxonium chloride. Thus addition of alcohol to an aqueous solution of the compound $[CrAn_2(AnH)Cl]$ leads to the reaction

$$[CrAn_2(AnH)Cl] + C_2H_5OH \rightleftharpoons [CrAn_3] + [C_2H_5OH_2]Cl, \qquad (10)$$

and the "oil" separating is contaminated with some $[CrAn_3]$, which is insoluble in alcohol.

Acetone is suitable for the separation of all compounds. Some of our compounds (such as $[CrGl(GlH)_2C_2O_4]$) are fairly soluble in glycol or glycerol, from which they may be reprecipitated by addition of excess of absolute alcohol; the product is a readily filtrable precipitate, and not the "oil" which would have been obtained from systems containing water. These precipitates are collected on a sintered glass filter, washed thoroughly with absolute alcohol, and dried to constant weight. Analysis of the precipitates shows that their structure is unaffected by this treatment.

General Review of Compounds

The group of compounds in which GlH or AnH molecules are coordinated with chromium may be considered as a special class of coordination compounds, having the following common properties: high solubility in water, high hygroscopicity, high viscosity of concentrated solutions, rising rapidly with rise in concentration, gradual transition from very viscous solutions to vitreous solids, insolubility in most organic solvents, property of separating as an "oil" from concentrated aqueous solutions on addition of excess of alcohol or acetone, tendency towards formation of polymeric multi-nuclear complexes, absence of crystalline structure in the solid state, and possession of marked acidic properties. Two other compounds, $[CrGl_2H_2OCl]$ and $[CrAn_2H_2OCl]$, have similar properties to the compounds of this class, although GlH or AnH molecules do not enter into their composition. However, the action of water on some of the glycine (alanine) cycles in aqueous solutions, causing their opening, confers upon these compounds some of the properties of the above class, although to a modified degree only.

The compounds with glycine are subdivided into groups, from diglycyl to hexaglycyl derivatives; the numerals (di-, tri-, etc) refer to the number of GlH molecules of Gl radicals entering into the composition of a given compound.

Table 1 below presents 11 types of glycine compounds of which we have prepared representatives. In the formulas X represents an acidic residue; we have prepared compounds in which X = Cl, or C_2O_4H, or $\frac{1}{2}C_2O_4$. We were not able to prepare compounds of the monoglycyl series (the compound $[CrGl(H_2O)_2C_2O_4]$ was actually obtained, but could not be isolated in a sufficiently pure form).

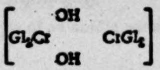
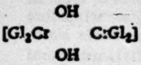
The Table also includes the internally complex salts $[CrGl_3]$ and  $\left[Gl_2Cr \overset{OH}{\underset{OH}{}} CrGl_2\right]$, which were taken as the starting point for preparation of all the other substances. All the types of compounds are genetically interconnected. The compounds from above down represent the products of the action of acids (opening of cycles), and from below up the products of the action of alkalis (closing of cycles); from left to right we have the products of replacement of H_2O or Cl by glycine.

TABLE 1

Series				
Diglycyl	Triglycyl	Tetraglycyl	Pentaglycyl	Hexaglycyl
 $[Gl_2Cr \overset{OH}{\underset{OH}{}} CrGl_2]$	$[CrGl_3]$			
$[CrGl_2H_2OX]$	$[CrGl_2(GlH)X]$	$[CrGl_2(GlH)_2]X$		
$[CrGl(GlH)H_2OX_2]$	$[CrGl(GlH)_2X_2]$	$[CrGl(GlH)_3X]X$		
$[Cr(GlH)_2H_2OX_3]$	$[Cr(GlH)_3X_3]$	$[Cr(GlH)_4X_2]X$	$[Cr(GlH)_5X]X_2$	$[Cr(GlH)_6]X_3$

Compounds of the di- and tri-glycyl series should formally be classed as non-electrolytes (tri-acido-triammine type), since all the component parts of the complex are included within the inner sphere, having zero charge. The initial internally complex salt $[CrGl_3]$ is a non-electrolyte, both in the formal sense and in reality; its molecular conductivity is very close to zero. The other compounds of the triacido-triammine type are converted into compounds of other types when dissolved in water, owing to their reactions with the solvent. The electrolytic dissociation of hydrated complexes (water is introduced into the inner sphere) is a result of this process.

Thus, for example, the chlorides of the triglycine series obtained from $[CrGl_3]$, viz., $[CrGl_2(GlH)Cl]$, $[CrGl(GlH)_2Cl_2]$, and $[Cr(GlH)_3Cl_3]$, are only in the formal sense non-electrolytes, since in aqueous solution replacement of inner sphere atoms of chlorine by water takes place, to give the corresponding 2-, 3-, and 4-ionic electrolytes $[CrGl_2(GlH)H_2O]Cl$, $[CrGl(GlH)_2(H_2O)_2]Cl_2$, and $[Cr(GlH)_3(H_2O)_3]Cl_3$. Moreover, owing to elimination of H ions from inner sphere GlH molecules the electro-conductivity of the solutions considerably exceeds that which would be expected from the structure of the hydrated complexes as given above.

Oxalates of the di- and tri-glycine series, such as $[CrGl(GlH)_2C_2O_4]$ and $[CrGl(GlH)H_2OC_2O_4]$, are much more nearly non-electrolytes, since the oxalic acid residues C_2O_4 are firmly held within the inner sphere. They too, however, owing to production of H ions from inner sphere GlH molecules, give solutions having a small (as compared with chlorides) electro-conductivity. Compounds such as $[Cr(GlH)_3(C_2O_4H)_3]$, which are formally non-electrolytes, in fact exhibit considerable electro-conductivity, since all of the inner sphere radicals (C_2O_4H and GlH) are able to produce H ions. Compounds of the tetra-, penta-, and hexa-glycyl series, such as $[Cr(GlH)_4Cl_2]Cl$, $[Cr(GlH)_5Cl]Cl_2$, and $[Cr(GlH)_6]Cl_3$, belong, respectively, to the diacido-tetrammine, the acido-pentammine, and the hexammine types, and are, with a tervalent central Cr atom, accordingly 2-, 3-, and 4-ionic electrolytes. Apart from this, they all form H ions from their inner spheres, so increasing the electro-conductivity of their solutions.

We see that a complex chain of reactions takes place in aqueous solutions of the substances under review.

We give below the more important of these transformations.

1. Replacement of inner sphere chlorine by molecules of water. As a result non-electrolytes become electrolytes, or the type of ionic dissociation changes .

$$[\cdots\text{Cr}-\text{Cl}]^0 + \text{H}_2\text{O} \rightleftarrows [\cdots\text{Cr}\text{---}\text{OH}_2]^{\cdot} + \text{Cl}^{\prime}. \qquad (11)$$

2. Coordinated molecules of amino-acids (GlH or AnH) are displaced, and replaced by water:

$$[\cdots\text{Cr}\text{---}\text{GlH}] + \text{H}_2\text{O} \rightleftarrows [\cdots\text{Cr}\text{---}\text{OH}_2] + \text{GlH}. \qquad (12)$$

Direct evidence of the existence of such processes is given by the separation, after long standing, from solutions of the complexes

$[CrGl(GlH)_2C_2O_4]$ and $[CrGl(GlH)H_2OC_2O_4]$

of the corresponding monoglycyl compound, of the composition $[CrGl(H_2O)_2C_2O_4]$.

3. Production of H ions takes place from inner sphere components of an acidic nature:

$$[\cdots\text{Cr}\text{---}\text{GlH}]^0 \rightleftarrows \text{H}^{\cdot} + \left[\cdots\text{Cr}\text{---}\overset{|}{\underset{|}{\text{Gl}}}\right]^{\prime}. \qquad (13)$$

Addition of alkali intensifies elimination of H ions, and the $\overset{|}{\text{Gl}}$ radicals so formed tend towards cycle closure, in some cases thereby giving internally complex salts.

4. Polymerization (association) takes place in concentrated solutions:

$$n[\cdots\text{Cr}\text{---}] \rightleftarrows [\cdots\text{Cr}_n\text{---}]. \qquad (14)$$

The result is that solutions of any of the compounds contain a large number of derived complex and simple particles.

Study of the physico-chemical properties of aqueous solutions of the compounds

It was found necessary to study the electro-conductivity, the acidity (pH), and the viscosity of their solutions in order to elucidate the nature of the above compounds, as well as to carry out cryoscopic determinations of their molecular weights. It is evident that when compounds possess considerable acidic properties the mere measurement of the electro-conductivity of their solutions cannot serve as a basis for making assumptions regarding their type of ionic dissociation, and for determining their coordination formulas. It is essential that pH measurements should be made at the same time as conductivity determinations. Having determined the pH, and so knowing the corresponding hydrogen ion concentration $[H^{\cdot}]$, it is necessary, knowing the mobility of H ions, to calculate their contribution to the value for molecular conductivity, which we shall designate as μ_H. The value of μ_H so found is subtracted from that found for molecular conductivity (μ), since it is only the difference ($\mu - \mu_H$) which is characteristic of the type of ionic dissociation of our complexes, and which can serve for the determination of their co-ordination formulas. Not only are H ions produced in acidic dissociation, but the charges of the complex radicals from which the H ions are eliminated undergo change. The effect of this change in the charge of the complex particles is, however, insignificant in comparison with that of the appearance of H ions, since the mobility of the large complex ions is, as we shall see, 12-14 times smaller than is that of H ions (25-30 mho per ion-equivalent at 25°, as compared with a mobility for H ions of about 350 mho. For this reason, the contribution due to acidic dissociation can in most cases be derived from the value of the contribution due to hydrogen ions, μ_H.

The values for the differences ($\mu - \mu_H$) for solutions of compounds containing chlorine in the inner sphere rise with time to a maximum, at which they remain constant. This effect is a consequence of gradual replacement of inner sphere chlorine by molecules of water, leading finally to an equilibrium of the type:

$$[\text{CrGl}_2(\text{GlH})\text{Cl}] + \text{H}_2\text{O} \underset{(a)}{\rightleftarrows} [\text{CrGl}_2(\text{GlH})\text{H}_2\text{O}]\text{Cl} \underset{(b)}{\rightleftarrows} [\text{CrGl}_2(\text{GlH})\text{H}_2\text{O}]^{\cdot} + \text{Cl}^{\prime}. \qquad (15)$$

In sufficiently dilute solutions (0.001M) the maximum values for $\mu - \mu_H$ correspond with complete transformation of the original complexes into the corresponding aquo-compounds. The maximum values for $\mu - \mu_H$ in 0.001M solutions of compounds containing 1 atom of chlorine in the inner sphere, such as, for example, $[CrGl_2(GlH)Cl]$ or $[CrGl_2(H_2O)Cl]$, amount to about 100 mho. Where there are two or three chlorine atoms within the inner sphere, such as in the compounds $[CrGl(GlH)_2Cl_2]$ or $[Cr(GlH)_3Cl_3]$, the maximum values of $\mu - \mu_H$ in 0.001M solutions are about 200 or 300 mho, respectively. The values of $\mu - \mu_H$ found correspond, respectively, with 2-, 3-, and 4-ionic electrolytes, such as, for example, $[CrGl_2(GlH)H_2O]Cl$, $[CrGl(GlH)_2(H_2O)_2]Cl_2$, and $[Cr(GlH)_3(H_2O)_3]Cl_3$, formed as a result of total replacement of chlorine from the inner sphere. Increase in the concentration of the solutions of compounds containing inner sphere chlorine leads to an abrupt fall in maximum values of $\mu - \mu_H$, which is due to diminution in the degree of hydration [a shift to the left of equilibrium (a) in equation (15)].

The values of $\mu - \mu_H$ found for chlorides such as $[CrGl_2(GlH)_2]Cl$ or $[Cr(GlH)_6]Cl_3$, which do not contain any inner sphere chlorine, do not change with time, nor are they greatly affected by changes in concentration. The constant value of $\mu - \mu_H$ for 0.001M $[CrGl_2(GlH)_2]Cl$ is 102 mho., which is the same as that of 0.001M solutions of chlorides with one chlorine atom in the inner sphere, such as $[CrGl_2(GlH)Cl]$ and others.

The values of $\mu - \mu_H$ in solutions of compounds not containing any chlorine, i.e., in the case of oxalates, such as, for example, $[CrGl(GlH)_2C_2O_4]$ or $[Cr(GlH)_3C_2O_4C_2O_4H]$ are close to zero. This shows that the conductivity of such solutions is due exclusively to acidic dissociation of inner sphere radicals; if this cannot take place the compounds are practically non-electrolytes.

The results of a study of the electro-conductivity of their solutions (allowing for acidic dissociation) confirm the coordination formulas arrived at for the compounds on chemical grounds.

Measurements of the conductivity of solutions of the compound $[CrGl_2(GlH)_2]Cl$ led to the determination of the mobility of the complex ion $[CrGl_2(GlH)_2]^+$, which was found to be about 27 mho. About the same value was found for the mobility of the other complex ions studied by us.

Measurements of the acidity (pH) of solutions of compounds belonging to one and the same series showed a regular increase in acidic properties as the number of glycine cycles opened rises. Thus, for example, the pH found for 0.001M solutions of $[CrGl_3]$, $[CrGl_2(GlH) Cl]$, $[CrGl (GlH)_2Cl_2]$ and $[Cr(GlH)_3Cl_3]$ were 7.06, 4.40, 3.97, and 3.56, respectively. It was found that, for compounds not containing Gl cycles, such as $[Cr(GlH)_3Cl_3]$, the change in $[H^+]$ due to varying the concentration agrees satisfactorily with the dilution law.

We have already mentioned that the concentrated aqueous solutions of the compounds described by us have an exceptionally high viscosity. We have studied the rise in relative viscosity (η) of the solutions as their concentration is increased from low to very high values. It appears that the relative viscosity of dilute solutions is of the order usually found for corresponding concentrations. The value of η rises sharply as the concentration increases. These findings are illustrated by Table 2, which gives relative viscosities for solutions of the monochloride of the triglycyl series, $[CrGl_2(GlH)Cl]$, at 25°.

TABLE 2

% in solution	6	31.0	18.6	53.3	58.0	63.8	66.1	70.0	73.7
η	1.14	2.31	10.0	15.3	28.0	127	237	560	5970

We determined the time of flow of the solutions applying different additional pressures, and found that Poiseuille's law is applicable to the solutions examined, which did not exhibit structural viscosity, characteristic of colloidal solutions. We investigated the relation between the composition of the compounds and the relative viscosity of their solutions at the same molar concentrations (7.62 molecules of water per molecule of dissolved substance, in all cases). The results are given in Table 3, for 11 compounds; η is relative to that of water, all at 25°.

We see in all three vertical columns that the value of η rises steeply with increase in the number of GlH molecules coordinated with chromium, i.e., with increase in the number of H_2O molecules or Cl atoms replaced by glycine. It is evident (horizontal rows) that increase in the number of molecules of GlH coordinated with chromium, and originating from opening of glycine cycles, is associated with increase in η as we pass from monochlorides (two Gl cycles) to dichlorides (one Gl cycle). Opening of the last Gl cycle, however, as seen in transition of dichlorides to trichlorides, leads to diminution of η (there is little further change in the tetraglycyl series).

The molecular weight of some of our compounds was determined by the cryoscopic method in aqueous solution. Since these compounds undergo electrolytic dissociation in aqueous solution it was necessary to determine not only the freezing point of the solutions, but also their pH and their conductivity, in order to allow for the contribution made by ions (Cl^-, H^+, and complex cations) towards the overall depression of freezing point.

We intend in a future paper to give a detailed description of the assumptions and methods used for the calculation, from the experimental data obtained for these complex cases, of the molecular weights of our coordination compounds. The complexity is due to the following: the non-electrolytes when in solution undergo conversion into electrolytes (e.g., $[CrGl(GlH)H_2OCl_2]$ into $[CrGl(GlH)(H_2O)_3]Cl_2$), and at the same time production of H ions from coordinated GlH molecules, displacement of coordinated GlH molecules by water, and polymerization processes take place in the solutions.

TABLE 3

Compound η		
$[CrGl_2(H_2O)Cl]$ 171	$[CrGl(GlH)(H_2O)Cl_2]$ 350	$[Cr(GlH)_2(H_2O)Cl_3]$ 222
$[CrGl_2(GlH)Cl]$ 500	$[CrGl(GlH)_2Cl_2]$ 1157	$[Cr(GlH)_3Cl_3]$ 665
$[CrGl_2(GlH)_2]Cl$ 675	$[CrGl(GlH)_3Cl]Cl$ 1645	$[Cr(GlH)_4Cl_2]Cl$ 1728
		$[Cr(GlH)_5Cl]Cl_2$ 3833
		$[Cr(GlH)_6]Cl_3$ 6708

It was found that the values obtained for molecular weight in dilute solutions are close to those expected for monomeric molecules. The molecular weights rise gradually with increasing concentration of the solutions. Table 4 gives the values found for freshly prepared solutions of the monochloride $[CrGl_2H_2OCl]$.

The molecular weight of the monomeric form of $[CrGl_2H_2OCl]$ should be 253.6, which is in fact found for 0.02 and 0.05M solutions. The value found is very considerably higher than the theoretical for 0.1M solutions and for 0.5M solutions it is 2.2 times greater than would be expected for the monomer. The dichloride $[CrGl(GlH)H_2OCl_2]$ is more highly polymerized in solution, the apparent molecular weight in 0.2M solution being 2030, which is 7 times greater than that of the monomer (290.05).

It was found that the values found for the molecular weights of compounds in solutions prepared from the solid substances diminish with time after dissolution, to become, in the case of not very concentrated solutions, finally constant, and close to the values for the monomers. The more concentrated is the solution, the more slowly is this final value achieved, and the more does it exceed that of the monomer. This is illustrated by the values for the molecular weight of $[CrGl(GlH)H_2OCl_2]$ found in 0.2M solutions at different times after dissolution, as given in Table 5.

TABLE 4

Concentration	0.02 M	0.05 M	0.067 M	0.1 M	0.2 M	0.5 M
Mol. wt.	252	248	289	358	417	563

The final value of 316 for the molecular weight remains constant, within the limits of experimental accuracy. The final value for 0.5M solutions was 375, after very prolonged standing; the molecular weight of the monomer is 290. The molecular weight of this same compound in solutions prepared in two different ways was compared. One solution (0.2M) was prepared in the usual way, by dissolving a weighed amount of solid $[CrGl(GlH)H_2OCl_2]$. For the second solution, the compound was synthesized by the reaction $[Cr_2Gl_4(OH)_2] + 4HCl \longrightarrow 2[CrGl(GlH)H_2OCl_2]$, in dilute solution, which was then concentrated in a vacuum desiccator to the required concentration of 0.2M. In the former solution, the molecular weight was at first 7 times greater than that of the monomer, gradually falling to 316. In the latter solution, the molecular weight found was 288, which coincides with that of the monomer; it did not change with time, and differs little from the final value obtained for the first solution (316).

It is thus evident that polymeric molecules are present only in solutions prepared from solid substances, and that these polymeric molecules gradually depolymerize in dilute solutions. If, however, the dilute solutions are prepared from compounds synthesized in even more dilute solution, and not isolated in the solid state, normal values are found for the molecular weights. We would add that the changes in the experimentally found values of molecular weight of compounds in passing from one group of them to another are paralleled by the changes in viscosity of their solutions.

Possible mechanism of polymerization of the compounds

The extremely high viscosity of concentrated aqueous solutions of the compounds, the continuous transition from highly viscous liquids, which can be drawn out as long, thin threads, to vitreous, non-crystalline solid phases, and other observations, suggested to us the possibility of presence of polymeric (associated) complexes in the solutions of the compounds prepared by us. Direct determination of their molecular weight by the cryoscopic method confirmed this supposition, and showed that depolymerization (dissociation of associated complexes) takes place when the solutions are diluted.

We suppose that, in concentrated solutions, the molecules of complexes containing $NH_2CHR \cdot COOH$ molecules (GlH, AlH) coordinated with chromium may be joined to each other by means of hydrogen bridges between free carboxylic groups of molecules of amino-acids coordinated with different atoms of chromium. Increase in the number of GlH molecules coordinated with a chromium atom (for example, in the trichloride series from $[Cr(GlH)_2H_2OCl_3]$ to $[Cr(GlH)_3]Cl_3$) should increase the probability of formation of hydrogen bridges between molecules of the corresponding compounds. This is confirmed indirectly by the increase in the relative viscosity of the solutions (of the same molarity) of the compounds under comparison observed when successive inner sphere chlorine atoms or water molecules are replaced by GlH molecules (see vertical columns of Table 3).

TABLE 5

Time of dissolution	15-20 min	3 hours	1 day	8 days	75 days
Mol. wt.	2030	1040	520	377	316

We also think it quite possible that, in addition to association due to joining together of different molecules by hydrogen bridges, some molecules may be associated through glycine bridges which join chromium atoms belonging to different molecules, as follows:

$$[\cdots Cr{-}{-}{-}NH_2CH_2COO{-}Cr{-}{-}{-}NH_2CH_2COO{-}Cr\cdots],$$

Such bridges might readily be formed in the following way. Molecules of water always enter the inner sphere of compounds in aqueous solution, and it is known that molecules of water coordinated with Cr^{+3} possess acidic properties, and are transformed into hydroxo-groups. The hydroxo-groups may react with GlH molecules coordinated with atoms of chromium belonging to other molecules, as follows:

$$[\cdots Cr{-}{-}{-}GlH] + [HO{-}Cr\cdots] \longrightarrow [\cdots Cr{-}{-}{-}Gl{-}Cr\cdots] + H_2O.$$

We suppose that it is in this way that unstable multi-nuclear complexes with glycine bridges are formed. Our study shows that all compounds containing glycine cycles can form multi-nuclear high molecular complexes without change in their empirical formula, i.e., they can form polymers. It is, however, evident that trichlorides of all series not containing glycine cycles cannot give rise to polymers with Gl bridges, and it is to this that we ascribe the fall in relative viscosity observed (see Table 3) in passing from dichlorides to trichlorides; trichlorides cannot form Gl bridges, although they are able to give rise to H bridges.

Received April 25, 1951

N.S.Kurnakov Institute of
General and Inorganic Chemistry,
Academy of Sciences USSR

LITERATURE CITED

[1] H. Ley and K. Ficken, Ber., 45, 377 (1912).

[2] A. A. Grinberg. Ann. Inst. Platinum, No. 8, 93 (1931).

[3] A. A. Grinberg and B. V. Ptitsyn. Ann. Inst. Platinum, No. 9, 55 (1932).

[4] A. A. Grinberg and L. M. Volshtein. Proc. USSR Acad. Sci. 7, 485 (1935).

[5] A. A. Grinberg and L. M. Volshtein. Bull. USSR Acad. Sci., Div. Chem. Sci., 1, 3 (1937).

[6] A. A. Grinberg and L. M. Volshtein. Bull. USSR Acad. Sci., Div. Chem. Sci., 4, 885 (1937).

[7] A. A. Grinberg. Proc. USSR Acad. Sci., 32, 57 (1941).

[8] A. A. Grinberg and L. M. Volshtein. Bull. USSR Acad. Sci., Div. Chem. Sci., 3, 381 (1941).

[9] L. M. Volshtein. Candidate's Thesis, Leningrad, 1937.

[10] L. M. Volshtein, Proc. USSR Acad. Sci., 48, 111 (1945).

[11] L. M. Volshtein, Proc. USSR Acad. Sci., 54, 323 (1946).

[12] L. M. Volshtein, J. Gen. Chem. 17, 2048 (1947).

[13] L. A. Chugaev and E. Serbin, Comptes. rend. 15, 119 (1912).

[14] L. Hugounenq and A. Morel, Comptes. rend. 15, 119 (1912).

[15] G. Florence and E. Couture, Bull. Soc. Chem. France, 39, 643 (1926)

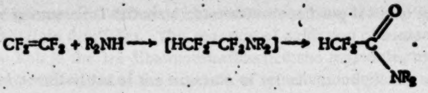
BLANK
PAGE

ADDITION REACTIONS OF PERFLUORO-OLEFINS

I. L. Knunyants and A. V. Fokin

Tetrafluoroethylene, trifluoroethylene, and other fluoro-olefins have certain specific chemical properties, shown in their ability to take part in reactions which are not characteristic of olefins, and in their low reactivity in typically olefin reactions. Tetrafluoro- and trifluorochloro-ethylene readily add on alcohols in presence of alkaline catalysts, to give the corresponding ethers [1]; thus tetrafluoroethylene and ethanol readily yield 1,1,2,2-tetrafluorodiethyl ether. Ethylene and other olefins do not react with alcohols under these conditions.

Tetrafluoroethylene readily reacts with amines, giving probably as the primary product a 1,1,2,2-tetrafluoroethylamine derivative, which cannot be isolated due to its ready hydrolysis, with production of N-substituted difluoroacetamide [2,3,4]



$$CF_2{=}CF_2 + R_2NH \longrightarrow [HCF_2{-}CF_2NR_2] \longrightarrow HCF_2{-}C(=O){-}NR_2$$

The reaction with ammonia proceeds similarly [4], giving difluoroacetonitrile, which polymerizes spontaneously to yield tri-(difluoromethyl)-triazine:

$$CF_2{=}CF_2 + NH_3 \longrightarrow [HCF_2{-}CF_2NH_2] \xrightarrow{-HF} [HCF_2{-}CN]_3.$$

Tetrafluoroethylene gives a number of products with sodium hydrogen sulfite [4], the most important being tetrafluoroethyl sulfonate and sodium difluoroacetate:

$$CF_2{=}CF_2 + NaHSO_3 \longrightarrow HCF_2{-}CF_2SO_3Na + HCF_2{-}COONa.$$

Formation of difluoroacetic acid is ascribable to the mobility of fluorine atoms, which are readily eliminated from the α-carbon atom during hydrolysis

$$HCF_2{-}CF_2SO_3Na \xrightarrow{H_2O} [HCF_2{-}COSO_3Na] + 2HF \longrightarrow HCF_2{-}COONa + SO_2 + 2HF.$$

It is evident from the examples given that tetrafluoroethylene reacts readily with substances which are of the nature of nucleophil reagents.

The reactions are in many cases, such as those with primary and secondary amines, associated with evolution of heat, whereas the corresponding reactions either do not proceed at all with ethylene, or do so only with considerable difficulty. Addition of halogens or of hydrogen halides to fluoro-olefins takes place with much greater difficulty than to olefins.

Fluoro-olefins are distinguished by a strong tendency towards polymerization; perfluorochlorovinyl and, under certain conditions, tetrafluoroethylene polymerize spontaneously when stored, and cases of the almost explosive polymerization of fluoro-olefins are known. Not enough is known, however, of the reactions of polymerization of fluoro-olefins to enable us to speak more definitely of their mechanism.

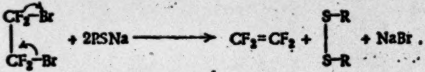
It may be concluded that it is owing to the electronophilic nature of polyfluoro-olefins that reactions with nucleophil reagents may be realized by an ionic, rather than by a radical, mechanism. The addition of nucleophil reagents, which are donors of electrons, to fluoro-olefins is related to the very high electronegativity of fluorine, which attracts electrons from the carbon atoms of fluoro-olefins. This causes weakening of the π-bond of tetrafluoroethylene, which for this reason is not able to participate in the reactions of addition typical of olefins, and, on the contrary, acquires a special affinity for nucleophil reagents.

A comparison of the chemical properties of tetrafluoroethylene with those of ethylene strengthens our view regarding the differences between the π-bonds of these substances, resulting from modification of the electron density of the bonds. The fluoro-olefin molecule is an acceptor of electrons, whereas ordinary olefins are donors thereof. It may in this connection be supposed that the initial process determining the reactions of tetrafluoroethylene is that of addition of the anion of the nucleophil reagent, which donates its electrons, and not the addition of cations, which is typical of reactions of addition to ethylene [5].

This supposition of addition of anions to tetrafluoroethylene is not without precedent; it is well known that compounds containing the carbonyl group (aldehydes, ketones) readily enter into reaction with nucleophil reagents, such as bisulfites, alcohols, ammonia, alkylamines, etc. These reactions begin with addition of anions to a carbon atom, functioning as a positive center [5].

The difficulty with which bromine adds on to tetrafluoroethylene (photo-activated reaction at 70-80°) is also ascribable to the special nature of its π-bond. As has been mentioned before, this circumstance is evidence of the attenuation of the π-bond in tetrafluoroethylene, and corresponds closely with the non-addition to tetraphenylethylene of bromine under the ordinary conditions. The weakening of the bond in tetraphenylethylene is due basically to conjugation of the electrons of the double bond with those of the benzene rings, together with an inductional effect.

We have shown that the structural peculiarities of tetrafluoroethylene are reflected in the properties of the products of addition to it of halogens. The reaction between sulfhydryl compounds and 1:2-dibromotetrafluoroethane or symmetrical difluorodichlorodibromoethane leads to regeneration of fluoro-olefins and to formation of the appropriate disulfides. This reaction of oxidation of mercaptans is evidence of the lability of the bromine-carbon link in the 1:2-dibromotetrafluoroethane molecule, and may be explained on the basis of the above-described peculiarities of the structure of tetrafluoroethylene, which lead to the polarization of this bond



$$CF_2Br{-}CF_2Br + 2RSNa \longrightarrow CF_2{=}CF_2 + RS{-}SR + NaBr.$$

The attenuation of the π-bond in perfluoro-olefins is the reason for the extreme instability of their dibromides, which are formed with difficulty, and which possess oxidative properties. Ethylene dibromide, on the contrary, reacts readily with mercaptans, with production of bisalkylethylene sulfides [6].

The powerful electronegative effect of fluorine is also frequently exerted on the π-bond; thus the C–C bond of hexafluoroethane is weakened as a result of abstraction of its electrons, and is broken by the action of bromine at raised temperatures, with production of two molecules of trifluorobromomethane [7]. This effect is closely analogous to the dissociation of hexaphenylethane, which contains six electron-attracting radicals. The affinity of fluorine for an electron is equal to 95 cal., and that of the phenyl group is much less, and if the dissociation were to be due to the induction effect only, hexaphenylethane would be expected to dissociate less readily than hexafluoroethane. In fact, however, hexaphenylethane dissociates more readily, since in the given case the effect of conjugation dominates.

A consideration of all these circumstances led us, in 1948 and 1949, to study the addition to fluoro-olefins of mercaptans, as typical nucleophil reagents. Various mercaptans reacted with tetrafluoroethylene, trifluorochloroethylene, or 1:1-difluoro-2:2-dichloroethylene in presence of alkaline catalysts, as follows:

$$CF_2{=}CF_2 + RSH \longrightarrow CF_2H{-}CF_2{-}S{-}R;$$

$$CF_2{=}CFCl + RSH \longrightarrow CFClH{-}CF_2{-}S{-}R;$$

$$CFCl{=}CFCl + RSH \longrightarrow CFClH{-}CFClH{-}S{-}R.$$

Of the three fluoro-olefins studied, the most reactive was found to be 1,1,2-trifluoro-2-chloroethylene (perfluorochlorovinyl). The high reactivity of $CF_2{=}CFCl$ is probably ascribable to the polarity of this reagent, since only such polarity, due to the asymmetrical structure of the molecule, could explain why addition of anions takes place preferentially at the carbon atom combined with fluorine only, i.e., at the atom with the smaller electron density. Similarly the products given by alkylamines with perfluorochlorovinyl are fluorochloroacetamides, not difluoroacetamides. As was expected, addition of ethylmercaptan to perfluorochlorovinyl does not take place in absence of catalysts or in presence of peroxides. In accordance with the views expressed above, addition takes place when the fluoro-olefin is heated under pressure with 3-5% of anhydrous sodium or potassium hydroxide, as catalyst.

Methyl, ethyl, and isopropyl mercaptan were thus made to react with perfluorochlorovinyl, to give methyl 1,1,2-trifluoro-2-chloroethyl sulfide, ethyl 1,1,2-trifluoro-2-chloroethyl sulfide, and 1,1,2-trifluoro-2-chloroethyl isopropyl sulfide, in 60-80% yields.

The sulfides so obtained were colorless, transparent, mobile liquids, with a characteristic unpleasant odor. Thiophenol reacts with perfluorochlorovinyl similarly to other mercaptans, giving phenyl 1,1,2-trifluoro-2-chloroethyl sulfide, in over 80% yield

$$CFCl{=}CF_2 + HS{-}C_6H_5 \longrightarrow CFClH{-}CF_2{-}S{-}C_6H_5.$$

The sulfide so obtained was purified by fractional distillation; it had a pleasant odor, resembling that of the products of addition of thiophenol to olefins.

Some of the sulfides prepared by us were converted by elimination of hydrogen fluoride into fluorovinyl sulfides. Individual products could not be obtained by elimination of hydrogen fluoride with alcoholic alkali, in the usual way, and all attempts at separating the complex mixture of products so obtained were unsuccessful. The only substance isolated in a pure state was the product of addition of amyl alcohol to the vinyl derivative obtained by elimination of hydrogen fluoride.

Better results were obtained by heating the initial saturated sulfide with anhydrous alkali at 110-130°, simultaneously distilling off the unsaturated product. Thus 1,1,2-trifluoro-2-chloroethyl ethyl sulfide gave 1,2-difluoro-2-chlorovinyl ethyl sulfide, b.p. 106-107°, a colorless liquid with a characteristic odor, and methyl 1,1,2-trifluoro-2-chloroethyl sulfide afforded 1,2-difluoro-2-chlorovinyl methyl sulfide, a transparent liquid of b.p. 88-89°:

$$C_2H_5{-}S{-}CF_2{-}CFClH \xrightarrow{-HF} C_2H_5{-}S{-}CF{=}CFCl$$

and

$$CH_3{-}S{-}CF_2{-}CFClH \xrightarrow{-HF} CH_3{-}S{-}CF{=}CFCl.$$

The properties of the products obtained are given in Tables 1,2 and 3.

EXPERIMENTAL

I. Methyl 1,1,2-trifluoro-2-chloroethyl sulfide. A mixture of 17 g of perfluorochlorovinyl, 8 g of methyl mercaptan, and 0.3 g of sodium hydroxide were heated for 6 hours at 115-125° in a stainless steel autoclave of 100 ml capacity. Unreacted olefin was distilled off, and the residue was washed with alkali and extracted with ether. The ethereal extract was distilled to remove solvent, and the residue was fractionally distilled, to give 10.6 g of pure product of b.p. 104°. Yield: 70% on reacted olefin.

The addition product, methyl 1,1,2-trifluoro-2-chloroethyl sulfide, is a transparent, mobile liquid with a specific odor. Analytical data, densities, and refractive indexes for this and other sulfides obtained similarly are given in Tables 1 and 2.

II. 1,2-Difluoro-2-chlorovinyl ethyl sulfide. A mixture of 10 g of ethyl 1,1,2-trifluoro-2-chloroethyl sulfide with 6.5 g of anhydrous potassium hydroxide is heated in a flask connected with a condenser, in an oil bath at 120-130°, collecting the unsaturated product of the reaction, which distils off at 105-107°. The distillate, after drying and redistillation, is 1,2-difluoro-2-chlorovinyl ethyl sulfide, b.p. 106-107°, a transparent, mobile liquid. Analytical and other data are given in Table 3.

III. Reaction of symmetrical tetrafluorodibromoethane or difluorodichlorodibromoethane with 2-hydroxyethyl mercaptan sodium salt.

1. Ten g of 2-hydroxyethyl mercaptan and 4.6 g of potassium hydroxide in 4 ml of water are placed in a round-bottomed flask fitted with a reflux condenser and a dropping funnel, and 13 g of warm symmetrical difluorodichlorodibromoethane (m.p. 34°) are added drop by drop. The addition of this substance is associated with considerable evolution of heat, with precipitation of KBr, and with copious evolution of a gas, which is condensed as a liquid in a receiver placed in a freezing mixture. After all of the dibromo-compound has been added the reaction mixture is heated for 1 hour at 60-65°. A total of 3.6 g of volatile liquid is collected in the receiver.

The residue in the flask is diluted with 30 ml of acetone, and is separated from the salt, the dry mass of which is 8.5 g. The acetone solution is dried with anhydrous magnesium sulfate, the acetone is distilled off, the residue is dissolved in chloroform, and the solution is treated with thionyl chloride. Excess of thionyl chloride and chloroform are distilled off, and the residue is fractionally distilled under reduced pressure. Four g of main fraction, b.p. 103-105°/2 mm, are obtained. The appearance and the characteristic odor of this product, as well as analytical and refraction data, show that it is identical with ethyl 2,2-dichloroethyl sulfide: d^{20} 1.341; n_D^{20} 1.5720, calculated MR_D 46.23, experimentally found MR_D 46.65 (previously described).

TABLE 1

Reagents		Addition product	Yield %	B.p. °C	d_4^t	n_D^t
Olefin	Mercaptan					
$CF_2=CFCl$	CH_3SH	$CH_3-S-C_2F_3ClH$	70	104	1.389/20°	1.4083/20°
Ditto	C_2H_5SH	$C_2H_5-S-C_2F_3ClH$	76-83	120/736	1.331/17°	1.4158/17°
"	$(CH_3)_2CHSH$	$(CH_3)_2CH-S-C_2F_3ClH$	74	135	1.275/20°	1.4178/20°
"	C_6H_5SH	$C_6H_5-S-C_2F_3ClH$	89	208	1.387/20°	1.5030/20°
$CF_2=CF_2$	CH_3SH	$CH_3-S-C_2F_4H$	75	63	1.322/8°	1.3675/8°
Ditto	C_2H_5SH	$C_2H_5-S-C_2F_4H$	60	88	1.246/18°	1.3735/18°
"	$(CH_3)_2CHSH$	$(CH_3)_2CH-S-C_2F_4H$	67	96	1.266/23°	1.3910/20°
"	C_6H_5SH	$C_6H_5-S-C_2F_4H$	76	64/12	1.3515/20°	1.4740/20°
$CFCl=CFCl$	CH_3SH	$CH_3-S-C_2Cl_2F_2H$	60	58.5/15	1.355/20°	1.5900/20°
Ditto	C_2H_5SH	$C_2H_5-S-C_2F_2Cl_2H$	62	138	1.425/20°	1.4612/20°
"	$(CH_3)_2CHSH$	$(CH_3)_2CH-S-C_2F_2Cl_2H$	52	159/738	1.302/25°	1.4534/20°
"	C_6H_5SH	$C_6H_5-S-C_2F_2Cl_2H$	78	93/3	1.400/20°	1.540/20°

NOTE: NaOH or KOH served as catalysts of the addition reactions. The duration of the addition reactions was from 3 to 6 hours.

TABLE 2

Formula	Mol. refraction		Sulfur, %		Fluorine, %		Chlorine, %	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
$CH_3-S-C_2F_3ClH$	28.47	29.14	19.50	20.09	34.55	34.05	21.57	22.18
$C_2H_5-S-C_2F_3ClH$	33.61	33.26	17.96	18.93	31.65	32.11	19.86	19.87
$(CH_3)_2CH-S-C_2F_3ClH$	37.72	38.03	16.55	16.80	29.60	23.03	18.41	18.66
$C_6H_5-S-C_2F_3ClH$	47.92	48.44	14.15	14.52	25.15	25.46	15.65	15.75
$CH_3-S-C_2F_4H$	23.77	23.96	21.62	22.04	51.35	51.14	–	–
$C_2H_5-S-C_2F_4H$	28.88	29.68	19.77	19.69	46.87	44.76	–	–
$(CH_3)_2CH-S-C_2F_4H$	32.90	33.30	18.10	18.32	43.00	43.26	–	–
$C_6H_5-S-C_2F_4H$	42.93	42.35	15.23	14.80	36.09	35.96	–	–
$CH_3-S-C_2F_2Cl_2H$	33.26	33.57	17.71	17.26	20.99	19.89	39.17	38.87
$C_2H_5-S-C_2F_2Cl_2H$	38.92	39.94	16.42	16.91	19.50	19.41	36.30	36.80
$(CH_3)_2CH-S-C_2F_2Cl_2H$	42.60	43.28	15.25	15.09	18.15	18.39	33.99	34.08
$C_6H_5-S-C_2F_2Cl_2H$	53.84	53.74	13.20	12.96	15.61	16.22	29.05	28.05
$C_2H_5-S-C_2F_2Cl$	32.65	32.58	20.21	19.81	23.97	24.94	22.36	21.70
$CH_3-S-C_2F_2Cl$	28.10	28.72	22.19	22.25	26.29	26.62	24.53	23.88
$CH_3-S-CFH-CFCl-O-C_3H_6$ . .	53.29	53.94	13.78	14.39	16.33	15.85	15.34	14.97

Found %: S 34.50; Cl 37.20.

$C_4H_6S_2Cl_2$. Calculated %: S 33.65; Cl 37.65

The volatile liquid collected in the receiver boiled at 22°, and was 1,2-difluoro-1,2-dichloroethylene. It was identified by treatment with bromine in a sealed steel cylinder at 50°, which gave a liquid product, most of which boiled at 42-45°/30 mm., and crystallized at 32-34°, mixed m.p. with difluorodichlorodibromoethane 34°.

Found %: F 12.98.

$C_2F_2Br_2Cl_2$. Calculated %: F 13.33

2. Eight g of tetrafluoro-1,2-dibromoethane is added gradually to 11 g of 2-hydroxyethyl mercaptan and 6 g of potassium hydroxide in 5 ml of water. The reaction mixture becomes hot, and gas is evolved. The gas (1.6 l) is condensed in a freezing mixture, and the condensate is treated with bromine in a steel cylinder, for 1 hour at 80-90°. The oil so obtained boiled at 48°.

Found %: F 30.43
$C_2F_4Br_2$. Calculated %: F 29.32

The reaction product was separated from the potassium bromide formed, and was purified as in the preceding experiment. Vacuum fractionation gave a product of b.p. 102-105°/2 mm., the absence of fluorine from which, together with the analytical and refraction data obtained, and with its characteristic odor, suggests that it is the same disulfide as was obtained in the preceding experiment.

Found %: S 34.95; Cl 37.94
$C_4H_8S_2Cl_2$. Calculated %: S 34.50; Cl 37.30

Calculated MR_D 46.23; experimentally found MR_D 45.96.

TABLE 3

Initial sulfide	Product of elimination of hydrogen fluoride	Yield, %	B.p. °C	d^{20}	n_D^{20}
$C_2H_5-S-C_2F_3ClH$	$C_2H_5-S-CF=CFCl$	90	106-107	1.282	1.4385
$CH_3-S-C_2F_3ClH$	$CH_3-S-CF=CFCl$	57	88-89	1.324	1.4390
$CH_3-S-C_2F_3ClH$	$CH_3-S-CFH-CFCl-OC_5H_{11}$	–	73/3	1.190	1.4640

SUMMARY

1. It has been shown that, owing to the lowering of the electronic density of the π-bond of tetrafluoroethylene it assumes an electronophilic nature, as a result of which it readily adds on nucleophil agents, in particular mercaptans.

2. A series of new fluorine-containing sulfides have been obtained from addition of methyl, ethyl, and isopropyl mercaptans, and of thiophenol to tetrafluoroethylene, perfluorochlorovinyl, or symmetrical difluorodichloroethylene.

3. Elimination of hydrogen fluoride from the fluorochloro-sulfides gave alkyl fluorovinyl sulfides.

4. The reaction between tetrafluorodibromoethane and alkyl mercaptides involves the oxidation of the latter, with formation of disulfides and of tetrafluoroethylene.

Received November 17, 1951

LITERATURE CITED

[1] J. Parc, D. Vail, J. Am. Chem. Soc. 70, 1550 (1948).

[2] W. Miller et al., J. Am. Chem. Soc. 70, 431 (1948).

[3] G. Rigby, H. Schroeder, Chem. Abs. 41, 987 (1947).

[4] D. Coffman et al., J. Org. Chem. 14, 747 (1949).

[5] D. Dewar, The Electronic Theory of Org. Chem., 1949.

[6] Roser, Reid, J. Am. Chem. Soc. 44, 632 (1922).

[7] Brice et al., J. Am. Chem. Soc. 71, 2999 (1949).

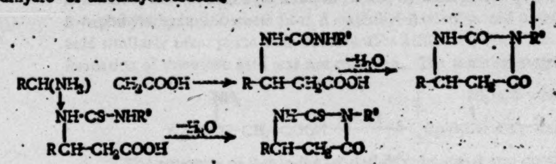
BLANK
PAGE

2-(2'-NAPHTHYL)-2-AMINOPROPIONIC ACID AND ITS PYRIMIDINE DERIVATIVES

PART 2

V. M. Rodionov and B. I. Kurtev

The corresponding ureido- or thioureido-derivatives are often prepared from β-amino-acids, for their identification. These derivatives readily eliminate one molecule of water, to give internal anhydrides, the so-called dihydro- or thiodihydrouracils



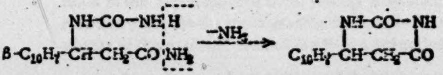
where R and R' = H, Alk, or Ar.

The ureido acids, dihydrouracils, and their sulfur-containing analogs are in most cases readily crystallizable substances, which are much less soluble in water than are the parent amino-acids. Very many of them possess specific biological activity, and their study is of considerable interest. Having previously prepared 2-(2'-naphthyl)-β-alanine in good yield [1], we have now prepared a number of pyrimidines characteristic of this substance.

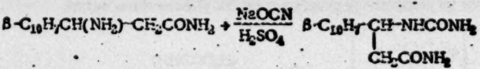
Three ureido-acids were synthesized, viz., 2-ureido-2-(2'-naphthyl)-propionic, 2-(ω-phenylureido)-2-(2'-naphthyl)-propionic, and 2-(N_1-methylureido)-2-(2'-naphthyl)-propionic acid, as starting products for the synthesis of the hexahydropyrimidines (dihydrouracils). The first of these substances was obtained in excellent yield by heating 2-naphthyl-β-alanine with urea in aqueous solution:

$$\beta\text{-}C_{10}H_7CH(NH_2)CH_2COOH + NH_2CONH_2 \longrightarrow \beta\text{-}C_{10}H_7CH(NHCONH_2)CH_2COONH_4.$$

It was found that the amide of the ureido acid was obtained as a by-product, in about 4% yield; its structure was established by hydrolyzing it to the free acid, and by converting it into naphthyldihydrouracil by heating the molten substance. Ammonia is evolved during this reaction:



Formation of amides of β-ureido-acids from β-amino acids and urea has not till now been reported, and, in fact, there is no mention of any such amides in the literature. The amide was, for this reason, also synthesized from β-naphthyl-β-alanine and sodium cyanate, in the usual way:



$$\beta\text{-}C_{10}H_7CH(NH_2)\text{-}CH_2CONH_2 + \frac{NaOCN}{H_2SO_4}\ \beta\text{-}C_{10}H_7\text{-}\underset{\displaystyle CH_2CONH_2}{\underset{|}{CH}}\text{-}NHCONH_2$$

β-(ω-phenylureido)-β-(β-naphthyl)propionic acid was prepared from β-naphthyl-β-alanine sodium salt and phenylisocyanate in aqueous solution:

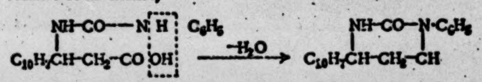
$$C_{10}H_7CH(NH_2)CH_2COONa + C_6H_5NCO \longrightarrow C_{10}H_7CH(NHCONHC_6H_5)CH_2COONa.$$

β-(N_1-methylureido)-β-naphthylpropionic acid was prepared from β-naphthyl-N_1-methyl-β-alanine and sodium cyanate in boiling aqueous solution.

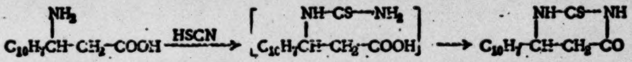
Conversion of the ureido acid and of N-methylureido acid into dihydrouracils is effected in good yield by boiling with dilute hydrochloric acid. Ring closure does not take place under these conditions with the ω-phenylureido acid, the reaction being one of full deamination, with formation of β-naphthylacrylic acid:

$$C_{10}H_7CH(NHCONHC_6H_5)CH_2COOH \longrightarrow C_{10}H_7CH{=}CH\text{·}COOH.$$

The appropriate phenylnaphthyldihydrouracil was prepared in small yield (30% of theory) by prolonged boiling of the phenylureido acid with dilute hydrochloric acid in methanol (10 parts by volume of 10% hydrochloric acid and 1 volume of methanol)

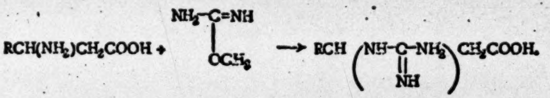


With stronger acid the sole reaction is methylation of the ureido acid. The tendency towards ring closure is lowered, and towards deamination raised, by attachment of a phenyl group to the nitrogen atom. Formation of β-naphthyldihydrothiouracil from β-naphthyl-β-alanine and potassium thiocyanate by heating with hydrochloric acid similarly takes place with considerable difficulty, the yield being less than 27%. The intermediate stage of formation of thioureido acid was not observed. The reaction proceeds as follows:



The structure of 2-thio-6-naphthyl-dihydrouracil was confirmed by its desulfuration, to give naphthyldihydrouracil. An attempt to prepare naphthyl-N-methylthiodihydrouracil analogously from β-naphthyl-N-methyl-β-alanine was unsuccessful, as deamination takes place, and only naphthylacrylic acid was separated from the reaction product.

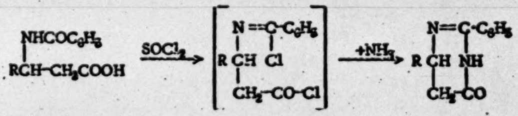
We have also investigated the possibility of preparation of amino (imino)-pyrimidines by ring closure of the appropriate guanidino acids. A number of methods of conversion of β-amino acids into β-guanidino acids have been studied in our laboratory, and we found, together with Urbanskaya [1], that the best method for preparation of β-guanidino derivatives is that based on the reaction between β-amino acids and O-methylisourea [1]:



Guanidination of β-(β-naphthyl)-β-alanine takes place with difficulty, the yield not exceeding 15%. This result is closely connected with Urbanskaya's earlier observation that β-amino acids with aliphatic radicals substituted in the β-position are more readily guanidinated than where the substituent is a phenyl group, and that the reaction proceeds the more readily the smaller is the molecular weight of the alkyl radical. The high molecular weight of the naphthyl radical leads to a reduction in the yield, to 15%.

Ring closure of guanidinonaphthylpropionic acid does not take place at all, the reaction being one of deamination with production of naphthylacrylic acid.

Zvorykina [2] has shown in an earlier paper from our laboratory that the amides of acyl derivatives of β-amino acids readily afford tetrahydropyrimidines by the following reactions:



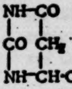
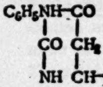
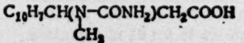
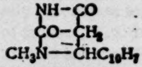
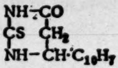
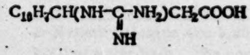
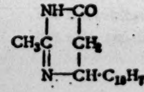
This reaction was performed with N-acetyl-β-naphthyl-β-alanine, giving 4-oxo-1-(β-naphthyl)-2-methyl-3,4,5,6-tetrahydropyrimidine.

The ureido acids and pyrimidine derivatives synthesized are given in the following Table.

EXPERIMENTAL

β-Ureido-β-(β-naphthyl)-propionic acid. 2.15 g of finely powdered β-(β-naphthyl)-β-alanine, 8 g of urea, and 45 ml of water are heated on a boiling water bath for 15 hours. The substrates gradually pass into solution, and after 2 hrs. the reaction mixture is a slightly turbid solution with a strongly ammoniacal odor. After cooling, 10 ml of 4% aqueous alkali should be added, in order to prevent possible premature separation of the ureido acid. The solution is filtered, in order to remove the insoluble residue which usually forms. The filtrate

TABLE

Formula and name	Yield %	M.p. of pure substance, °C
$C_{10}H_7CH(NHCONH_2)CH_2COOH$ β-Ureido-β-(β-naphthyl)-propionic acid	92.5	199-199.5 with foaming
$C_{10}H_7CH(NHCONH_2)CH_2CONH_2$ β-Ureido-β-(β-naphthyl)-propionamide	80	217.5 with decomposition
 6-(β-naphthyl)-dihydrouracil	73	245-246
$C_{10}H_7CH(NHCONHC_6H_5)CH_2COOH$ β-(ω-Phenylureido)-β-(β-naphthyl)-propionic acid	87	178.5-179.5 with foaming
$C_{10}H_7CH(NH\cdot CONHC_6H_5)CH_2COOCH_3$ Methyl β-(ω-phenylureido)-β-(β-naphthyl)-propionate	89.5	142-143
 3-Phenyl-6-(β-naphthyl)-dihydrouracil	30	233-234
 $C_{10}H_7CH(N(CH_3)-CONH_2)CH_2COOH$ β-N-Methylureido-β'-(β'-naphthyl)-propionic acid	30	180-181 with foaming
 6-(β'-Naphthyl)-1-methyldihydrouracil	70	200.5-201.5
 β-Thio-6(β'-naphthyl)-dihydrouracil	27	261-261.5
 $C_{10}H_7CH(NH-C(=NH)-NH_2)CH_2COOH$ β-Guanidino-β-(β-naphthyl)-propionic acid	15	249-250
 4-Oxo-6-(β-naphthyl)-2-methyl-3,4,5,6-tetrahydropyrimidine	59.5	127.5-129

is extracted a few times with ether, and the aqueous residue is made acid to Congo red with hydrochloric acid. The voluminous precipitate is collected on the filter pump, washed with water, and dried on a porous tile and then in an oven at 70°. The yield is 2.38 g (about 92.5% of theoretical), and the product melts at 196-197°, with foaming. The dry product is recrystallized from alcohol, when the m.p. rises to 199-199.5°, with characteristic foaming. The ureido acid is not soluble in ether, benzene, or cold water, slightly soluble in boiling water, rather more soluble in cold concentrated hydrochloric acid, and readily soluble in dilute alkalis. It is difficultly soluble in cold methanol or ethanol, but very soluble in the boiling solvents; solubilities in acetone are similar, but somewhat lower.

Found %: C 64.89; 65.14; H 5.19; 5.28; N 10.48; 10.45.
$C_{14}H_{14}O_3N_2$. Calculated %: C 65.4; H 5.42; N 10.85.

The residue obtained by filtration of the alkalized reaction solution is dissolved in boiling alcohol, and the solution is filtered while hot from insoluble impurities. Silky colorless crystals separate from the filtrate on cooling; the yield is 0.11 g (4.2% of theoretical), m.p. 213.5° (with decomposition). The properties of this product, and the analytical data obtained for it show that it is β-ureido-β-(β-naphthyl)-propionamide.

When heated with aqueous alkali the substance dissolves readily, with evolution of ammonia, and addition of acid to the cooled solution causes precipitation of a compound of m.p. 196-197° (with foaming), which does not depress the m.p. of β-ureido-β-(β-naphthyl)-propionic acid. The substance evolves ammonia when heated at the m.p. in a test-tube, and the molten product rapidly crystallizes. The solid so obtained is recrystallized from alcohol, to give a product of m.p. 244-245°, mixed m.p. with pure 6-(β-naphthyl)-dihydrouracil 245°. The substance does not depress the m.p. of β-ureido-β-(β-naphthyl)-propionamide, prepared from the amide of β-(β-naphthyl)-β-alanine and sodium cyanate.

Found %: C 65.59; 65.72; H 5.81; 5.64; N 16.29; 16.47.
$C_{14}H_{15}O_2N_3$. Calculated %: C 65.37; H 5.83; N 16.34.

β-Ureido-β-(β-naphthyl)-propionamide. A solution of 0.215 g of the amide of β-(β-naphthyl)-β-alanine and 0.072 g of sodium cyanate in 7.6 ml of about 2% sulfuric acid is heated for 5-10 min. on a boiling water bath, and the crystalline precipitate separating from the cooled solution is collected on the filter pump. The yield of product, m.p. 216°, is 0.20 g, i.e., about 80% of theoretical. All the properties of the product coincide with those of the amide obtained as a by-product of the synthesis of β-ureido-β-(β-naphthyl)-propionic acid.

β-(ω-phenylureido)-β-(β-naphthyl)-propionic acid. Phenylisocyanate (0.68 g) is added drop by drop, with constant stirring, and cooling the reaction vessel with ice, to a solution of 1.08 g of β-(β-naphthyl)-β-alanine in 10 ml of 4% aqueous sodium hydroxide. After a few hours the reaction mixture is diluted with water and filtered. The filtrate is extracted with ether, and is made acid with dilute hydrochloric acid. The oily precipitate separating solidifies after a few hours, when it is collected, washed and dried at 70°. The yield of product, m.p. 160.5-170.5° (with foaming), is 1.45 g (87% of theoretical); after crystallization from aqueous alcohol and then from alcohol alone the m.p. rises to 178.5-179.5° (with foaming). The substance crystallizes in colorless prisms, and is insoluble in ether or benzene, fairly soluble in cold alcohol or acetone, and very soluble in hot alcohol or acetone. It is insoluble in water or mineral acids, and is readily soluble in aqueous alkalis.

Found %: N 8.73; 8.81.
$C_{20}H_{18}O_3N_2$. Calculated %: N 8.38.

β-(N_1-methylureido)-β-(β-naphthyl)-propionic acid. A mixture of 0.38 g of β-(β-naphthyl)-β-N-methylalanine and 0.20 g of sodium cyanate (85% excess) in 10 ml of water is heated for 4 hours on a boiling water bath. The cooled solution is filtered, and dilute hydrochloric acid is added to a strongly acid reaction to Congo red. The voluminous precipitate is collected, washed with water, and dried first on a porous tile and then in an oven at 70°; yield 0.32 g (about 72% of theoretical). After two recrystallizations from alcohol the substance has m.p. 180-181°; it is sparingly soluble in cold alcohol or acetone, but more soluble in the hot solvents, insoluble in ether, benzene, water, or mineral acids, and readily soluble in aqueous alkalis.

Found % : N 10.28; 10.34.
$C_{15}H_{16}O_3N_2$. Calculated %: N 10.29.

6-(β-Naphthyl)-dihydrouracil. A solution of 2.58 g of β-ureido-β-(β-naphthyl)-propionic acid in 100 ml of concentrated hydrochloric acid (d 1.18) is boiled for 30 min., the precipitate which separates from the cooled solution is collected, washed with water, and dried at 70°. The product, weighing 2.33 g, and melting indefinitely at 225-234°, is treated with boiling ethanol (50 ml), the suspension is filtered hot, and the residue is washed on the filter with two further small portions of hot ethanol; the m.p. is thus raised to 244-245°. After one more recrystallization from a large volume of alcohol 1.10 g of analytically pure product are obtained, m.p. 245-246°; the alcoholic filtrate yields a further 0.55 g of this substance. The total yield is 1.65 g, i.e., 73% of theoretical.

Naphthyldihydrouracil crystallizes in small colorless prisms, often joined in rosettes. It is sparingly soluble in the ordinary organic solvents, not very soluble in boiling alcohol, and insoluble in water or mineral acids. It is fairly readily hydrolyzed by boiling 4-5% aqueous alkalis, to ureidonaphthylpropionic acid

Found %: C 70.20; H 4.48; N 12.04, 12.12.
$C_{14}H_{12}O_2N_2$. Calculated %: C 70; H 5.0; N 11.66.

Attempted ring closure of β-(ω-phenylureido)-β-(β-naphthyl)-2-propionic acid.

1. Boiling the phenylureido-naphthyl-propionic acid with hydrochloric acid gives β-(β-naphthyl)-acrylic acid in practically theoretical yield.

2. Boiling with hydrochloric acid and methanol leads to formation of methyl-β-(ω-phenylureido)-β-(β-naphthyl)-2-propionate.

A mixture of 0.66 g of β-phenylureido-β-naphthylpropionic acid, 20 ml of methanol, and 5 ml of concentrated hydrochloric acid (d 1.18) is boiled for 5 hours on a water bath, the solution is cooled, and water is added. The precipitate separating is collected after 3 hours, washed with water, and dried at 70-80°; yield 0.66 g of substance of m.p. 136.5-140.5° (about 89.5% of theoretical). After recrystallization from aqueous alcohol the m.p. rises to 142-143°.

The methyl ester crystallizes from aqueous alcohol in the form of colorless prisms, insoluble in water, alkalis, or acids, readily soluble in acetone, sparingly soluble in cold, but readily soluble in hot, benzene or alcohol, and sparingly soluble in ether. It is rapidly hydrolyzed by dilute alkalis to the corresponding acid.

Found %: C 74.42; 72.34; H 5.66; 5.73; N 7.81; 7.83.
$C_{21}H_{20}O_3N_2$. Calculated %: C 73.39; H 5.75; N 8.04.

3. Preparation of 3-phenyl-6-(β-naphthyl)-dihydrouracil. A mixture of 1.67 g of β-(ω-phenylureido)-β-(β-naphthyl)-propionic acid, 100 ml of 16% hydrochloric acid, and 10 ml of methanol is boiled for 15-20 hrs. on the water bath. Visible dissolution of the initial acid is not observed. The cooled reaction mixture is filtered, giving a residue of 1.12 g of a substance, m.p. 182-207°, which is dissolved in a large volume of boiling alcohol. The solution on cooling deposits 0.47 g of crystalline product (30% of theoretical yield), m.p. 232-233°, raised by repeated crystallization to 233-234°.

3-Phenyl-6-(β-naphthyl)-dihydrouracil crystallizes in short colorless prisms. It is difficultly soluble in water, alkalis, acids, ether, benzene, and cold alcohol, and sparingly soluble in boiling alcohol. It is readily hydrolyzed by boiling dilute alkalis to phenylureidonaphthylpropionic acid.

Found %: C 75.63; 75.57; H 5.31; 5.13; N 8.99.
$C_{20}H_{16}O_2N_2$. Calculated %: C 75.92; H 5.10; N 8.86

6-(β-naphthyl)-1-methyldihydrouracil. A suspension of 0.54 g of β-(N-methylureido)-β-(β-naphthyl)-propionic acid in 24 ml of dilute hydrochloric acid (1:1) is heated for 90 minutes on a boiling water bath; dissolution of the substance is not seen to take place. The cooled suspension is filtered, and the residue is washed with water and dried at 100°. The yield of crude product, m.p. 190-195°, is 0.5 g; the m.p. rises to 196-199° after one recrystallization from alcohol, and further purification is effected by dissolving in boiling alcohol, and adding two volumes of ether, when 0.38 g (70% of theoretical) of pure product, m.p. 200.5-201.5°, separates.

6-(β-Naphthyl)-1-methyldihydrouracil crystallizes in thick prisms. It is insoluble in cold, and slightly soluble in hot, water, and is more soluble in alcohol than in water, and even more so in acetone. It is insoluble in ether. The substance is rapidly hydrolyzed by hot alkalis.

Found %: C 71.07; 71.26; H 5.57; 5.61; N 11.09; 11.29.
$C_{15}H_{14}O_2N_2$. Calculated %: C 70.85; H 5.55; N 11.02.

2-Thio-6-(β-naphthyl)-dihydrouracil. A mixture of 2.15 g of β-(β-naphthyl)-β-alanine, 1.52 g of potassium thiocyanate, and 1 ml of concentrated hydrochloric acid in 15 ml of water is evaporated to dryness on a water bath, and the powdered residue is heated on the oil bath at 145-150° for 2-3 hrs. The cooled product is heated for 10 min at 100° with 20 ml of 4% hydrochloric acid, and the residue is collected, washed with water, and dried. The product, weighing 1.72 g, melts at 144-197° (with partial decomposition at about 160°). Neutralization of the filtrate with sodium acetate gives 0.38 g (17.7% of the weight of β-naphthyl-β-alanine taken) of unreacted initial substance.

The product of m.p. 144-197° is dissolved in 130 ml of boiling alcohol, and the solution is cooled, when a substance containing sulfur and nitrogen separates, m.p. 239-241.5°, yield 0.57 g, i.e. 22% on total, or 27% on reacted, naphthyl-β-alanine. Repeated recrystallizations finally gave a product of m.p. 261-262.5°, analysis of which showed that it is still not quite pure.

Found %: N 10.52; 10.56; S 11.81; 12.01
$C_{14}H_{12}ON_2S$. Calculated %: N 10.93; S 12.51

2-Thio-6(β-naphthyl)-dihydrouracil is insoluble in ether or benzene, sparingly soluble in cold alcohol or acetone, and readily soluble in hot alcohol and acetone. It is insoluble in water or mineral acids, but is easily dissolved without decomposition in alkaline solutions.

Conversion into 6-(β-naphthyl)-dihydrouracil. A small amount of 2-thio-6-(β-naphthyl)-dihydrouracil is heated for 25 hrs. with a large excess of lead acetate in aqueous alcoholic solution, after which the alcohol and some of the water are distilled off, and the cooled residual solution is filtered. The black residue on the filter is repeatedly extracted with small amounts of boiling alcohol, and the combined extracts are stood for 24 hours, to give a deposit of small prisms, joined in rosettes, of m.p. 245-246°, not depressing the m.p. of a sample of 6-(β-naphthyl)-dihydrouracil, prepared by a different method, but giving a considerable depression of the m.p. of 2-thio-6-(β-naphthyl)-dihydrouracil, to 220°.

All attempts at preparing 2-thio-6(β-naphthyl)-1-methyl-dihydrouracil by a similar method were unsuccessful, the deamination produce β-(β-naphthyl)-acrylic acid being obtained in all cases.

β-Guanidino-β-(β-naphthyl)-propionic acid. A solution of 5.94 g of O-methylisourea hydrochloride (m.p. 117-118°) in 30 ml of anhydrous methanol is cooled in a freezing mixture, and added to a similarly cooled solution of 1.35 g sodium in 30 ml anhydrous methanol. The sodium chloride separating out after 15 minutes is filtered off, and is washed with cooled anhydrous methanol. The clear solution of O-methylisourea so obtained is added to 6.45 g of finely powdered β-(β-naphthyl)-β-alanine, followed by 50 ml of water and about 300 ml methanol, with mechanical stirring. The reaction proceeds very slowly, the β-amino acid does not dissolve for a long time, and the solution is stirred mechanically for 15 days. The methanol is then distilled off under reduced pressure, on a water bath at 40-50°. The first parts of the distillate have a strong ammonia odor. The precipitate separating after elimination of methanol is collected after a day, and washed with small amounts of water; the yield is 1.27 g, m.p. 233-236° (with decomposition). A small amount of substance of m.p. 126.5-129.5° separated from the filtrate on the following day; the amount was too small to permit of its examination. The product, of m.p. 233-236°, is dissolved in dilute hydrochloric acid, the solution is extracted several times with ether, and excess of concentrated ammonia is added. The precipitate forming is collected and washed with water; yield 1.17 g (about 15% of theoretical), m.p. 238-240° (with decomposition), rising to 249-250° (with decomposition), when recrystallized from aqueous alcohol. β-Guanidino-β-(β-naphthyl)-propionic acid, is a finely crystalline powder readily soluble in cold dilute acids and in boiling aqueous alcohol, but difficulty soluble in cold water and alcohol.

Found %: N 16.46; 16.25; 16.34.
$C_{14}H_{15}O_2N_3$ Calculated %: N 16.33

All attempts towards the cyclization of guanidinonaphthylpropionic acid were unsuccessful, as deamination took place when it was heated with hydrochloric acid, to give β-naphthylacrylic acid in good yield.

4-Oxo-6-(β-naphthyl)-2-methyl-3,4,5,6-tetrahydropyrimidine. A mixture of 1.28 g of N-acetyl-β-(β-naphthyl)-β-alanine (m.p. 226-228°), with 8 ml of acetic anhydride is heated for 8 hrs on an oil bath at 140°. The excess of acetic anhydride is distilled off under reduced pressure on an oil bath at about 130°, the last traces being decomposed by boiling with 25 ml of water for 20-30 min.; a small amount of crystalline material separates from the aqueous solution on cooling. The oily residue in the flask is extracted with a small amount of benzene, after which it crystallizes. The crystalline product, together with that separating from the aqueous solution, is wetted with alcohol and is shaken for 1 hour with 10 ml of cold 2% alkali. The insoluble residue is collected on a filter, washed with water, and dried. The yield is 0.71 g (58-60% of theoretical) of substance of m.p. 124-126°, raised to 127.5-128° by recrystallization from water.

4-Oxo-6-(β-naphthyl)-2-methyl-3,4,5,6-tetrahydropyrimidine crystallizes from water as needles. It is very soluble in alcohol, chloroform, or hot benzene, and fairly soluble in cold ether or benzene. It is very soluble in concentrated, but only sparingly soluble in dilute, hydrochloric acid or in aqueous alkali at room temperature. When recrystallized from water it retains it tenaciously, and requires prolonged drying in a desiccator before being analyzed.

Found %: C 75.57; 75.40; H 6.08, 6.22; N 11.89; 11.93.
$C_{15}H_{14}ON_2$. Calculated %: C 75.60; H 5.92; N 11.76.

The alkaline filtrate obtained during purification of the product was made acid with dilute hydrochloric acid, when 0.02 g of the initial N-acetyl-β-(β-naphthyl)-β-alanine separated out.

SUMMARY

1. β-Ureido-β-(β-naphthyl)-propionic acid, β-(ω-phenylureido)-β-(β-naphthyl)-propionic acid, and β-(N_1-methylureido)-β-(β-naphthyl)-propionic acid have been prepared, and have been converted into the corresponding 2,4-dioxo-hexahydropyrimidine derivatives 6-(β-naphthyl)-dihydrouracil, 3-phenyl-6-(β-naphthyl)-dihydrouracil, and 6-(β-naphthyl)-1-methyl-dihydrouracil.

2. Its amide was formed as a by-product of preparation of β-ureido-β-(β-naphthyl)-propionic acid, and was also synthesized from β-amino-β-(β-naphthyl)-propionic acid and sodium cyanate.

3. β-Ureido-β-(β-naphthyl)-propionamide undergoes cyclization when heated.

4. Methyl-β-(ω-phenylureido)-β-(β-naphthyl)-propionate has been prepared.

5. 2-Thio-6-(β-naphthyl)-dihydrouracil, β-guanidino-β-(β-naphthyl)-propionic acid, and 4-oxo-6-(β-naphthyl)-2-methyl-3,4,5,6-tetrahydropyrimidine have been synthesized.

Received August 31, 1951

D. N. Mendeleev
Chemico-Technological Institute

LITERATURE CITED

[1] V. M. Rodionov and B. I. Kurtev. Bull. USSR Acad. Sci., Div. Chem. Sci., 1, 113 (1952). *

[2] V. M. Rodionov and O. S. Urbanskaya. J. Gen. Chem., 18, 2023 (1948).

[3] V. M. Rodionov and V. K. Zvorykina. Bull. USSR Acad. Sci., Div. Chem. Sci., 216 (1943); 330 (1948); V. M. Rodionov and V. V. Kiseleva. J. Gen. Chem., 18, 1912 (1948).

---

* See Consultants Bureau English translation, p. 123.

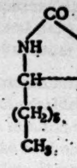
BLANK
PAGE

SYNTHESIS OF β-AMINO-β-CYCLOHEXYLPROPIONIC ACID AND OF SOME OF ITS DERIVATIVES

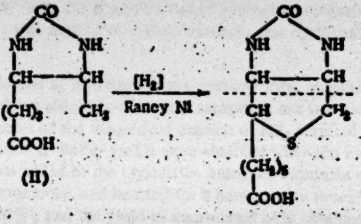
V. M. Rodionov and T. S. Kiseleva

The method of synthesis of β-amino acids discovered in our laboratory in 1926, depending on condensation of aromatic aldehydes with malonic acid in presence of alcoholic ammonia [1], has recently been extended to aldehydes of the aliphatic and naphthalene series [2], and preliminary experiments have been made on its application to heterocyclic aldehydes [3]. It was for certain reasons of importance to extend the method to aldehydes of the cyclane group. The synthesis of β-amino acids with cyclic substituents in the β-position would be of interest not only for merely preparative reasons.

We have, together with Zvorykina [4], shown that β-aminopelargonic acid (β-hexyl-β-alanine) is a biologically active substance, which similarly to β-alanine, although to a much smaller degree, stimulates the growth of yeast. A particularly interesting biologically active substance, possessing biotin activity, is hexylglyoxalidone (I), which is easily prepared from β-aminopelargonamide by the Hoffman reaction. The structure of this substance is very similar to that of desthiobiotin (II), a degradation product of the universal growth factor biotin (III).



(I)

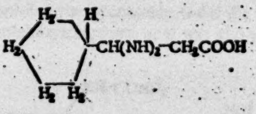


(II)

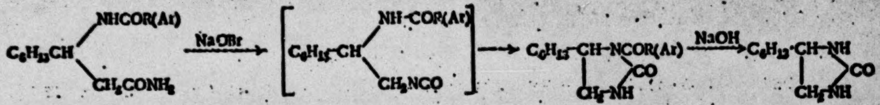
(III)

The glyoxalidone ring is seen to be a part of the molecule of these three biologically active substances, and it seems that the activity of these compounds depends largely on the presence of this heterocyclic system, since desthiobiotin (II) differs very little from biotin in its activity, which is also little affected by methylating the carboxylic group. This activity requires the presence in position 4(5) of the ring of a C_6 substituent. However, replacement of hexyl by phenyl leads to total loss of biotin activity, as was shown by a microbiological study of phenylglyoxalidone, prepared in 1932 by Kanevskaya [5].

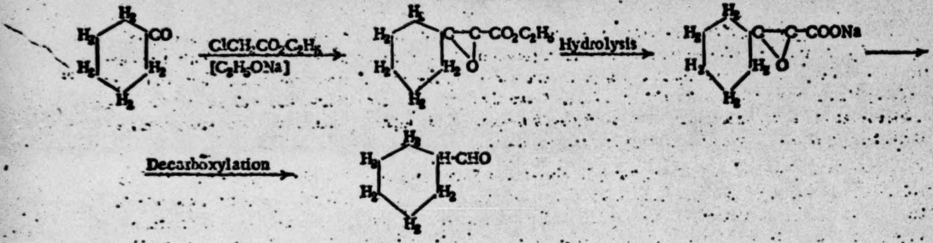
It was of very great interest to find what is the effect of substituting cyclohexyl for phenyl in both β-aminopropionic acid and in the corresponding glyoxalidone derivative, for the preparation of which it was necessary to study the Hoffmann reaction with β-cyclohexyl-β-alanine.



We have since 1943 been conducting in our laboratory a systematic study of the reaction between acylated amides of β-amino acids and hypobromite, from which it appears that the chief product of the reaction is a 4(5)-substituted glyoxalidone, formed through the intermediate stage of acylglyoxalidone, first isolated by Zvorykina [4]: (see top of next page). The study of cyclohexyl-β-aminopropionic acid is thus of interest both for confirmation of the mechanism of formation of 4(5)-glyoxalidone derivatives, and for the elucidation of the biological activity of the acid itself and of the derived cyclohexylglyoxalidone.



In order to prepare β-amino-β-cyclohexylpropionic acid by our method it was first necessary to work out a convenient method for preparation of hexahydrobenzaldehyde. A number of published methods were tested, and it was found that the best results were given by that involving decomposition of the ester obtained from monochloroacetic ester and cyclohexanone [6].

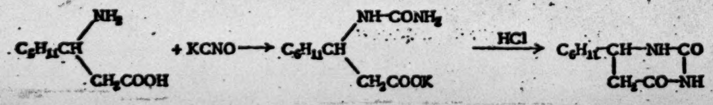


Hexahydrobenzaldehyde was obtained by us as the crystalline aldehyde-ammonia derivative of m.p. 104-105° (see experimental part). The same reaction was applied to cyclopentanone, and cyclopentylformaldehyde was obtained in somewhat lower yield.

Condensation with malonic acid was at first done in the ordinary way. Alcoholic ammonia was added to hexahydrobenzaldehyde, and the crystalline aldehyde-ammonia separating out was heated with malonic acid. The ammonia solution was taken in 10% excess of the theoretical amount of NH_3 required for the reaction. The yield of β-amino acid amounted to 50% of theory. Better yields were obtained when the excess of alcoholic ammonia, with absolute alcohol as the solvent, was added to the crystalline aldehyde-ammonia compound. Very good results were obtained taking a 40% excess of ammonia, and heating for 8 hours on the water bath. Under these conditions the yield of amino acid was raised to 66%, and the yield of unsaturated acid obtained as a by-product was reduced to 11% of theoretical.

The reaction of condensation of hexahydrobenzaldehyde with malonic acid differs from that with aromatic aldehydes in that two isomeric unsaturated acids are obtained, one with the double bond in the α-β-position (cyclohexylacrylic acid, $C_6H_{11}CH=CH{\cdot}COOH$), and the second with a γ-double bond (cyclohexylidenepropionic acid, $C_6H_{10}=CH\ CH_2COOH$). The unsaturated acid separated by us was completely identical with cyclohexylacrylic acid, described in 1928 by Sircar [7] and by Venus-Danilova [8] in 1934.

The N-acetyl-, N-benzoyl-, and N-carbomethoxy-derivatives of β-amino-β-cyclohexylpropionic acid, and their amides, were prepared, and the Hoffmann reaction was carried out with all of these acylated amides. The N-benzoyl and N-carbomethoxy amides gave cyclohexylglyoxalidone, together with its N-benzoyl or N-carbomethoxy derivative; this affords further confirmation of the mechanism proposed by us for the Hoffmann reaction with β-amino acids [4]. β-Acetamido-β-cyclohexylpropionamide under the same conditions gives only cyclohexylglyoxalidone, however. β-Ureido-β-cyclohexylpropionic acid was also synthesized, and the appropriate cyclohexyldihydrouracil was prepared from it.

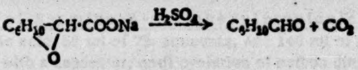


EXPERIMENTAL

Preparation of cyclohexylglycidic ester. Into a three-necked flask fitted with a stirrer, a reflux condenser, and a thermometer are placed 49 g of cyclohexanone ($\frac{1}{2}$ mole), 61 g of ethyl monochloroacetate, and 100 ml of dry benzene; the mixture is cooled to 0°, and sodium ethoxide powder is added in small portions*, from a sealed extension connected with the flask by rubber tubing; the rate of addition of sodium ethoxide is regulated by the temperature of the reaction mixture, which should not exceed 15°. After the whole of the sodium ethoxide has been added, the contents of the flask are stirred for 4 hrs., and are allowed to stand for 48 hrs. at room temperature, when the flask is placed on a boiling water bath, and the mixture is diluted with water. A benzene solution of the glycidic ester separates. The lower, aqueous layer is twice extracted with benzene, and the combined benzene extracts are washed successively with water, with 3% acetic acid, and again with water, and are then dried with anhydrous sodium sulfate. After distilling off the benzene, the residual glycidic ester is fractionally vacuum distilled, collecting the fraction boiling at 115-116°/10 mm; yield 67 g, i.e., 73% of theoretical. The reaction proceeded much faster when sodamide was substituted for sodium ethoxide, but the yield fell to 50%.

Hydrolysis of the cyclohexylglycidic ester. 67 g of ester are added gradually to a solution obtained by adding 9.2 g of sodium to 220 ml of absolute alcohol. The slightly turbid solution is cooled to 15°, and 8 ml of water is added, causing considerable heating, and being followed by precipitation of sodium salt of glycidic acid. The precipitate is collected on the next day, and washed with 30 ml of absolute alcohol followed by 30 ml of ether, and dried at 120°; yield 57.6 g, i.e., about 90% of theoretical.

Preparation of hexahydrobenzaldehyde, and its conversion into aldehyde-ammonia compound. This stage of the synthesis, viz., separation of aldehyde obtained by decomposition of glycid salt



$$C_6H_{10}\!-\!CH\cdot COONa \xrightarrow{H_2SO_4} C_6H_{10}CHO + CO_2$$

is the most difficult, since the free aldehyde readily polymerizes on standing, and is very quickly converted in the presence of mineral acids into crystalline metahexahydrobenzaldehyde [9]. The following procedure was designed to prevent this undesirable reaction: sulfuric acid was taken instead of the usual hydrochloric acid, and was added gradually to the sodium salt of the glycidic acid, in a current of steam. The hexahydrobenzaldehyde was thus removed from the acid medium as soon as it was formed, so greatly reducing polymerization.

A solution of 250 g of sodium salt of the glycidic acid in 150 ml of water is placed in a three-necked flask, and 150 ml of 1:1 sulfuric acid is added gradually through a dropping-funnel, steam being passed through the solution at the same time. The hexahydrobenzaldehyde distilling over is collected in ice-water, the upper layer is collected, dissolved in 50 ml of alcohol, and the solution is saturated with ammonia, with violent shaking and good cooling. The crystalline aldehyde-ammonia compound separating is left with the ammoniacal solution for 10-12 hrs, after which it is collected, washed with small portions of alcohol, and dried on a porous tile, and then in a vacuum desiccator; yield of aldehyde-ammonia compound, m.p. 104-105°, 47.7 g, a further 4 g of which was obtained by evaporating the alcoholic mother liquor under reduced pressure. The aqueous condensate (800 ml) is redistilled giving 300 ml of distillate containing aldehyde, from which a further 13.5 g of aldehyde-ammonia, m.p. 103-104°, is obtained. The total yield is 65.2 g, or about 42% of theoretical.

The compound so obtained does not contain oxygen, and its analysis gives the formula $(C_7H_{13}N)_x$, i.e., it is an aldimine. It crystallizes in bundles of thin needles, melting at 104-105°, with decomposition. It is readily soluble in benzene (1:6) sparingly soluble in ether, and practically insoluble in water. At room temperature 0.1 g of the aldimine does not dissolve in 10 ml of alcohol, but it passes into solution at 60°, not crystallizing out again, however, when the solution is cooled; the aldimine evidently decomposes when heated, to yield free aldehyde. This view is confirmed by the observation that when the cooled alcoholic solution is again saturated with ammonia it gives a precipitate of the same aldimine crystals, m.p. 104-105° (after drying). This behavior of the aldimine was used for its purification by recrystallization.

Found %: C 75.31; 75.21; H 11.85; 11.88; N 12.71; 12.75.
$C_7H_{13}N$. Calculated %: C 75.67; H 11.71; N 12.61.

---

* In our first experiments we prepared the sodium ethoxide in the usual way, from absolute alcohol and sodium in an atmosphere of nitrogen, but in the later experiments we used sodium ethoxide made by the Scientific Research Institute for Synthetic Perfumes from alcohol and sodium hydroxide, which was not less active than our preparation. We are deeply indebted to the Deputy Director of this Institute, Prof. V. N. Belov, for supplying us with this reagent.

Preparation of cyclopentylformaldehyde. Cyclopentanone was prepared by the method of Thorpe and Kon [10], and was converted into the cyclopentylglycidic ester. For this purpose, 42 g of cyclopentanone, 61 g of ethyl monochloroacetate, and 100 ml of benzene were placed in a three-necked flask fitted with a reflux condenser, a stirrer, and a thermometer, and sodamide was added gradually, with constant stirring, in a freezing mixture at −2°. The temperature gradually rises, but should not exceed 15°. Stirring is continued for 2 hrs., after which the yellowish-brown reaction mixture is poured on ice. The benzene layer is separated from the aqueous layer, which is twice extracted with 100 ml portions of benzene. The combined benzene extracts are washed twice with water, once with 3% acetic acid, again with water, and dried over anhydrous sodium sulfate. The benzene is distilled off, and the residue is fractionally distilled at 20 mm pressure, collecting the fraction distilling over at 119-122°; the yield is 29.1 g of practically pure glycidic ester, i.e., about 33.7% of theoretical.

The ester is very readily hydrolyzed by warming its alcoholic solution with sodium ethoxide. The sodium salt so obtained is converted into cyclopentylformaldehyde by the same method as for hexahydrobenzaldehyde, by heating with sulfuric acid in a stream of steam, collecting the aldehyde distilling off in ice-water. The distillate is extracted with ether, the ethereal extract is dried with anhydrous sodium sulfate, and the ether is distilled off. The residue is fractionally distilled under reduced pressure, collecting the fraction boiling at 40-43°/17 mm, which was fairly pure aldehyde; yield 40% of theoretical for the amount of sodium salt taken.

Preparation of β-amino-β-cyclohexylpropionic acid. A mixture of 34.9 g of crystalline aldimine, 28.3 g of malonic acid, 28 ml of 7% ammonia, and 140 ml of alcohol was heated for 8 hrs on a water bath, in a flask connected with a condenser, until evolution of carbon dioxide ceased. Complete dissolution of the substrates does not take place; the white mass gradually shrinks, and turns yellow at the edges, as the alcohol distills off. After completion of the reaction the product is extracted a few times with hot water, when most of it goes into solution, leaving a viscous yellow oil at the bottom of the flask. The aqueous extract is separated, made acid with acetic acid, and extracted with ether, and the ethereal extracts are added to the oil. The solution, thus separated from unreacted aldehyde and from unsaturated acid, is evaporated down until a crystalline crust appears on the surface. The crystalline deposit forming after long standing at low temperature is collected, washed with cold water, in which it is very sparingly soluble, and dried, to give 25.4 g of crystalline product, m.p. 215-216°. Evaporation of the mother liquor gives a further 10.25 g., melting at 211-212°.

The total yield is 35.65 g., or 66% of theoretical calculated on aldimine taken. β-Amino-β-cyclohexylpropionic acid is readily soluble in alkalis, alcohol, or hot water, difficultly soluble in cold water, and insoluble in ether. After recrystallization from alcohol it melts at 217-218°.

Found %: C 62.93; 62.74; H 9.83; 9.83; N 8.40; 8.37.
$C_9H_{17}O_2N$. Calculated %: C 63.15; H 9.93; N 8.18.

Isolation of cyclohexylacrylic acid. The ethereal extract obtained in the preceding experiment is washed with aqueous bisulfate, to remove traces of aldehyde, and then with water, and is dried over anhydrous sodium sulfate. The ether is distilled off, leaving a yellow, viscous oil with a pungent odor like that of the lower fatty acids. The oil is readily soluble in light petroleum, alcohol, ether and alkalis, but only sparingly soluble in hot water; it may be purified by steam distillation. It crystallizes after long standing in a desiccator containing calcium chloride. The crystals, m.p. 51-53°, are vacuum distilled, to give a colorless, rapidly crystallizing oil, b.p. 153-155°/10 mm., m.p. 56-57°, not changed by recrystallization from alcohol; yield 4.7 g; i.e., about 11% of theoretical, calculated on aldimine taken.

Found %: C 69.69; 69.70; H 9.15; 9.20.
$C_9H_{14}O_2$. Calculated %: C 70.10; H 9.10.

Preparation of β-benzamido-β-cyclohexylpropionic acid. A solution of 10 g of β-amino-β-cyclohexylpropionic acid in 92 ml of 10% sodium hydroxide is treated with constant stirring with 8.2 g of benzoyl chloride added gradually from a dropping funnel. Stirring is continued for another 3 hours, after which the solution is made strongly acid to Congo red with hydrochloric acid. The oil which separates very quickly crystallizes, giving a product which is practically insoluble in cold water, and sparingly soluble in hot water, alcohol, or ether. It is freed of benzoic acid by extracting twice with boiling water, and filtering the hot suspension. The filtrate deposits a small amount of a mixture of benzoic acid and N-benzoyl derivative, m.p. 130-131°. The residue after removal of benzoic acid was dried at 120°, when it melted sharply at 193.5-194°; yield 13.5 g, or 84.5% of theory. The melting point rises to a maximum value of 197-198° after two recrystallizations from alcohol.

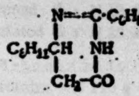
Found %: N 5.24; 5.10

$C_{16}H_{21}O_3N$. Calculated %: N 5.09

Preparation of β-benzamido-β-cyclohexylpropionamide. A solution of 11.8 g of β-benzamido-β-cyclohexylpropionic acid in 16.9 g of thionyl chloride in a flask fitted with a reflux condenser is heated at 40° until evolution of gas ceases; the reaction is usually completed within 1½ to 2 hours. The excess of thionyl chloride (three times the theoretical amount) is distilled off under reduced pressure (about 12 mm). The acid chloride crystallizing out is dissolved in 600 ml of ether, to give a bright yellow solution, which is saturated for two hours with dry ammonia, with cooling. The precipitate forming is collected, washed with 5% sodium hydroxide solution and then with water, and then recrystallized from alcohol; the yield of pure amide, m.p. 252-253°, was 5.5 g, or 47% of theoretical.

The ethereal mother liquor is decolorized by boiling with active charcoal, the solution is filtered, and the ether is distilled off, leaving 0.77 g of substance of m.p. 160.5-162°, rising to 165-165.5° after recrystallization from alcohol. The substance crystallizes in long, thin needles, which are readily soluble in ether or hot alcohol, but not in water, dilute acids, or alkalis.

The reactions and properties of the substance are identical with those of the tetrahydropyrimidine derivative 4-oxo-2-phenyl-6-cyclohexyltetrahydropyrimidine.



Zvorykina [5], working in our laboratory on the synthesis of compounds of this sort, usually prepared them by heating the benzoyl derivatives with thionyl chloride at 70-80°, whereas in our case the reaction was conducted at 40-45°. The fact that it proceeds under such mild conditions is evidence of the strong tendency of cyclohexyl-amino acid derivatives towards ring-closure. The elementary analysis of the compound obtained by us also confirms the correctness of our supposition.

Found %: C 74.64; 74.83; H 7.93; 8.0; N 10.66; 10.84.

$C_{16}H_{20}ON_2$. Calculated %: C 75.00; H 7.81; N 10.93.

Preparation of β-carbomethoxyamino-β-cyclohexylpropionic acid. Twelve g of methyl chloroformate is added gradually, during an hour, to a cooled solution (0-2°) of 20 g of amino acid in 190 ml of 10% sodium hydroxide, with constant stirring, which is continued for a further 3 hours, after which hydrochloric acid is added to a distinctly acid reaction to Congo red. An oily deposit forms, which soon crystallizes, and which is collected after 10-12 hours, washed with water, and dried at 90°. The carbomethoxy derivative so obtained is fairly pure, m.p. 143-145°, raised to 145.5-146.5° by one recrystallization from alcohol; yield 22 g, or 82% of theoretical.

Found %: N 6.35; 6.20.

$C_{11}H_{19}O_4N$. Calculated %: N 6.11.

Preparation of the amide. A mixture of 7.9 g of β-carbomethoxyamino-β-cyclohexylpropionic acid and 11.8 g of thionyl chloride is heated at 40° for 3 hrs., until evolution of gas practically ceases, when excess of thionyl chloride is distilled off under reduced pressure. The residual crystalline substance is suspended in ether, in which it is practically insoluble, and the suspension is saturated with ammonia, giving a voluminous precipitate of amide, which is collected after 10-12 hours, washed with 5% sodium hydroxide solution and with water, and dried at 100°. The product melts at 170-175°, and after recrystallization it has m.p. 192-193°, yield 6.5 g, or 82.3% of theoretical. It is sparingly soluble in cold, and readily soluble in hot alcohol.

Found : N 12.44; 12.29.

$C_{11}H_{20}O_3N_2$. Calculated : N 12.28.

Preparation of β-acetamido-β-cyclohexylpropionic acid. Ten g of acetic anhydride is added gradually, with constant stirring, to 10 g of amino acid in 93 g of 12% aqueous potassium hydroxide at 2-3°, stirring is continued for a further 2 hrs, and hydrochloric acid is added until the solution is distinctly acid to Congo red. It is then evaporated down, and placed in a cool room. The crystalline product which separates after long standing is collected, washed with cold water, and dried; yield 6.5 g, m.p. 159-160°.

Recrystallization from water gives long flat prisms, m.p. 164.5-165.5°. The mother liquor is evaporated to dryness, the residue is extracted with a small amount of dilute alkali, the extract is filtered, and the filtrate is made acid with hydrochloric acid, giving a further 1.1 g of acetyl derivative, m.p. 160.5-161.5°. The total yield is 7.6 g, or 61% of theory.

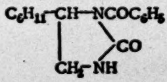
Found %: N 6.62; 6.54.
$C_{11}H_{19}O_3N$. Calculated %: N 6.57.

β-Acetamido-β-cyclohexylpropionamide. 5.9 g of acetyl derivative and 11.5 g of thionyl chloride are heated at 40° in a flask fitted with a reflux condenser. After 2 hrs, during which the substance partly dissolves, and gas is evolved, the excess of thionyl chloride is distilled off, and the crystalline residue of acid chloride is suspended in ether, in which it is practically insoluble. The suspension is saturated with dry ammonia, with vigorous shaking and thorough cooling, and the resulting amide is collected, washed with 5% aqueous sodium hydroxide and then with water, and recrystallized from alcohol; bundles of small needles, m.p. 228-229°, yield 1.9 g, or 32% of theoretical.

Found %: N 13.0; 12.95.
$C_{11}H_{20}O_2N_2$. Calculated %: N 13.2.

Hoffmann reaction with β-benzamido-β-cyclohexylpropionamide. A solution of hypobromite prepared from 9.4 g of bromine and 110 g of 15% aqueous potassium hydroxide is cooled to 10°, 7 g of β-benzamido-β-cyclohexylpropionamide is added, and the mixture is stirred at −2 to 0° for 3 hrs. Complete dissolution of the amide does not take place, and the solution still remains turbid after gentle heating on the water bath to 45°, at which temperature the suspended matter coagulates. The flask is then removed from the water bath, but its temperature rises without further heating from 48° to 65°. It is then quickly cooled, when a precipitate separates, which is collected, washed with water, and dried, giving 4.57 g of product melting indefinitely at 196-204°. Two recrystallizations from alcohol give four substances:

1) 2.54 g of substance of m.p. 216.5-217.5°; thin needles insoluble in water, ether, benzene, dilute alkalis and mineral acids, soluble in alcohol and acetic acid. The properties of this substance, and its analytical data, show that it is 1-benzoyl-5-cyclohexylglyoxalidone:



The substance was obtained in 36% yield. (2.54 g).

Found %: C 70.77; 70.59; H 7.44; 7.29; N 10.24; 10.30.
$C_{16}H_{20}O_2N_2$. Calculated %: C 70.58; H 7.39; N 10.29.

2) 0.17 g of substance of m.p. 205-206°, after recrystallization from alcohol m.p. 215-215.5°, platelets, soluble in dilute hydrochloric acid (1:1) and in alcohol, insoluble in ether and in alkalis. Analysis of this substance showed that it is 5-cyclohexylglyoxalidone; yield about 4% of theoretical.(0.17 g).

Found %: C 64.14; 64.21; H 10.18; 10.10; N 16.65; 16.68.
$C_9H_{16}ON_2$. Calculated% : C 64.28; H 9.52; N 16.67.

3) 0.22 g of a substance of m.p. 242-243°, identical with the initial amide, the mixed m.p. with which gives no depression. Yield 3% .

4) 0.63 g of a dark-colored, uncrystallizable oil, which was not further studied, owing to the small amount available.

The alkaline mother liquor was treated with bisulfite, and was made acid with hydrochloric acid. The precipitate forming was collected, washed with water, and recrystallized; it melted at 119-120°, and was identical with benzoic acid (yield 0.36 g). Part of the N-benzoyl-cyclohexylglyoxalidone separating in the reaction (0.74 g) was hydrolyzed by heating on a boiling water bath with 20% aqueous sodium hydroxide.

N-Benzoyl-cyclohexylglyoxalidone is insoluble in alkalis, and is only difficultly wetted by water; at the beginning of the reaction it floats on the surface, and only towards the completion of heating does it sink to the bottom of the flask, as a finely crystalline deposit, which is collected, washed with water, and dried;

yield 0.46 g of substance of m.p. 175-183°, raised to 215-215.5° by one recrystallization from alcohol. It does not depress the m.p. of cyclohexylglyoxalidone.

Under the above conditions only about 70-80% of the substance is hydrolyzed, part of it being recovered unchanged. Ether extraction of the acidified solution gives 0.26 g of benzoic acid (78-79% of theoretical).

The Hoffmann reaction was conducted similarly with acetamidocyclohexylpropionamide, which readily dissolves in alkaline hypobromite. The spontaneous rise in temperature is not so great in this case, not exceeding 32°. The oily product soon crystallizes, giving a substance melting indefinitely at 174-178°. Recrystallization from alcohol gives pure cyclohexylglyoxalidone, m.p. 215-215.5°. No intermediate product of the reaction could be isolated, suggesting that it must be very unstable in alkaline solution.

The yield of cyclohexylglyoxalidone from 1 g of amide was 0.35 g, or 44% of theoretical. Acidification of the alkaline solution, followed by ether extraction, gave 0.1 g of brown oil, which was not further investigated.

Hoffmann reaction with N-carbomethoxyamino-β-cyclohexylpropionamide. 2.76 g of amide is added, with stirring, to a hypobromite solution prepared by adding 5.2 g of bromine to 5 g of potassium hydroxide in 33 g of water. Stirring is continued for 1½ to 2 hrs at −2° to 0°, to complete dissolution of the amide, when the flask is transferred to a water bath at 80°. A sudden rise in temperature is observed at 42° to 60° and a voluminous crystalline precipitate forms; at the same time the yellow color of the solution disappears. The suspension is cooled quickly, filtered, and the precipitate is washed with water, and treated with ether, which dissolves only the oily part of the precipitate leaving the crystalline part, which is washed with water and dried; yield of product melting at 153-155° 0.31 g. After washing with hydrochloric acid and recrystallizing from alcohol the m.p. rises to 159.5-160.5°. Analysis of this product shows that it is N-carbomethoxycyclohexylglyoxalidone.

Found % : C 58.94; 59.01; H 7.53; 7.69; N 12.57; 12.63.
$C_{11}H_{18}O_3N$. Calculated % : C 58.40; H 7.96; N 12.39.

The ethereal solution is washed with 1:1 hydrochloric acid, and the ether is then distilled off, to give 0.45 g of an oily residue, which crystallizes on standing in a desiccator. The crystalline product is dissolved in ether, the solution is washed with aqueous alkali, and the ether is distilled off, leaving 0.38 g of a crystalline residue of m.p. 158-160°, not depressing the m.p. of pure carbomethoxycyclohexylglyoxalidone, the total yield of which was thus 0.69 g, or 28% of theoretical.

The dilute hydrochloric acid used for washing the ethereal solution is made alkaline with caustic potash, when 0.13 g of cyclohexylglyoxalidone (6.5% of theoretical) is obtained. Increasing the concentration of alkali leads to reduction in the yield of acylated glyoxalidone. Thus with double the amount of potassium hydroxide the yield of carboxymethyl derivative falls to 4%, and of cyclohexylglyoxalidone rises to 53%.

Preparation of β-ureido-β-cyclohexylpropionic acid. A mixture of 2 g of amino acid and 1.5 g of potassium cyanate in 40 ml of water is heated for 4 hrs on a briskly boiling water bath. After completion of the reaction the solution is cooled, and hydrochloric acid is added to a distinctly acid reaction to Congo red. The gelatinous precipitate is collected and recrystallized from aqueous alcohol; yield 0.75 g (30%) of rosettes of crystals of ureidocyclohexylpropionic acid, m.p. 165-166° (with decomposition)

Found %: N 13.29; 13.14.
$C_{10}H_{18}O_3N_2$. Calculated %: N 13.09.

Preparation of 6-cyclohexyldihydrouracil. 0.3 g of ureido-acid is boiled for 30 min with 100 ml of hydrochloric acid (d 1.12), and the clear solution is evaporated down to small volume. The crystalline precipitate forming from the cooled solution is collected, washed with a small amount of water, and recrystallized from alcohol, to give 0.1 g of cyclohexyldihydrouracil, m.p. 225-226°; yield 36.5%.

Found %: N 14.15; 14.28.
$C_{10}H_{16}O_2N_2$. Calculated %: N 14.28

SUMMARY

1. Rodionov's method for synthesis of β-amino acids has been extended to aldehydes of the alicyclic series.

2. A simple method of preparation of hexahydrobenzaldehyde or cyclopentylformaldehyde from cyclohexyl-

or cyclopentyl- glycidic ester, respectively, is described.

3. Condensation of hexahydrobenzaldehyde with malonic acid leads to formation of β-amino-β-cyclohexylpropionic acid, in 50% yield.

4. The yield of β-amino acid is raised to 66% when the aldimine is taken for the condensation instead of the free aldehyde.

5. The N-benzoyl-, N-acetyl-, and N-carbomethoxy- derivatives of β-amino-β-cyclohexylpropionic acid and its amide are described, as well as β-ureodi-β-cyclohexylpropionic acid and cyclohexyldihydrouracil.

6. The Hoffmannreaction is carried out with the acylated derivatives of the aminopropionamides, and it is shown that the N-benzoyl- and N-carbomethoxy- derivatives give 5-cyclohexylglyoxalidone and its N-benzoyl- or N-carbomethoxy- derivatives.

β-Acetamido-β-cyclohexylpropionamide gives only cyclohexylglyoxalidone when treated with hypobromite.

7. The formation of acylated cyclohexylglyoxalidones confirms the correctness of the mechanism proposed by Rodionov and Zvorykina [4] for the Hoffmann reaction of β-amino acids.

Received August 31, 1951

D.I. Mendeleev Chemical-Technological Institute

LITERATURE CITED

[1] V. M. Rodionov and E. F. Malevinskaya, Ber. 59, 2952 (1926); V. M. Rodionov and E. A. Postovskaya, J. Am. Chem. Soc. 51, 841, (1929).

[2] V. M. Rodionov and N. G. Yartseva, Bull. USSR Acad. Sci., Div. Chem. Sci. 1, 103(1952);* V. M. Rodionov and N. G. Kurtev, Bull. USSR Acad. Sci., Div. Chem. Sci., 1, 113 (1952).**

[3] V. M. Rodionov and T. K. Veselovskaya. J. Gen. Chem. 20, 2203 (1950).***

[4] V. M. Rodionov and V. K. Zvorykina, Bull. USSR Acad. Sci. Div. Chem. Sci. 3, 216 (1943).

[5] S. I. Kanevskaya. J. prak. Chem. (II) 132, 335 (1932).

[6] G. Darzens, P. Lefebure, Comptes. rend. 142, 714 (1906).

[7] Sarbrani Sahay Guha Sircar, J. Chem. Soc. 54 (1928).

[8] E. D. Venus-Danilova, J. Gen. Chem. 4, 868 (1934).

[9] N. D. Zelinsky and I. F. Gutt. Ber. 40, 3052 (1907).

[10] Syntheses of Organic Reagents, Vol 1, p. 518 (GIIL, 1949).

---

*See Consultants Bureau translation, p. 113.

**See Consultants Bureau translation, p. 123.

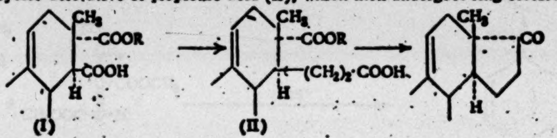
***See Consultants Bureau translation, p. 2887.

SYNTHESIS OF POLYCYCLIC COMPOUNDS RELATED TO THE STEROIDS. XI

RESEARCHES ON THE STEREOCHEMISTRY OF CYCLIC COMPOUNDS. I. CONDENSATION OF DIVINYL WITH CITRACONIC AND MESACONIC ACID AND THEIR ESTERS. CIS-TRANS-ISOMERISM OF 1-METHYLCYCLOHEXANE-1,2-DICARBOXYLIC ACIDS AND THEIR ESTERS

I. N. Nazarov and V. F. Kucherov

One of the possible ways of building up polycyclic systems related to the steroids may be through the synthesis of cyclic-trans-dicarboxylic acids (I), with subsequent building up of a side-chain to give the corresponding cyclic derivative of propionic acid (II), which then undergoes ring closure, as follows:



This method was successfully applied by Bachmann [1] for the simplest case of synthesis of cis- and trans-8-methylhydrindan-1-one.

However, the methods given in the literature for synthesizing even the simplest cis- and trans-1-methylcyclohexane-1,2-dicarboxylic acids do not give adequate yields of pure product [2]. Even more difficult to prepare are cis- and trans-1-methylcyclohexane-1-carboxy-2-acetic acid [3] or -2-propionic acid [4]. It was for this reason necessary first of all to work out new, more convenient methods of synthesis of compounds of this sort.

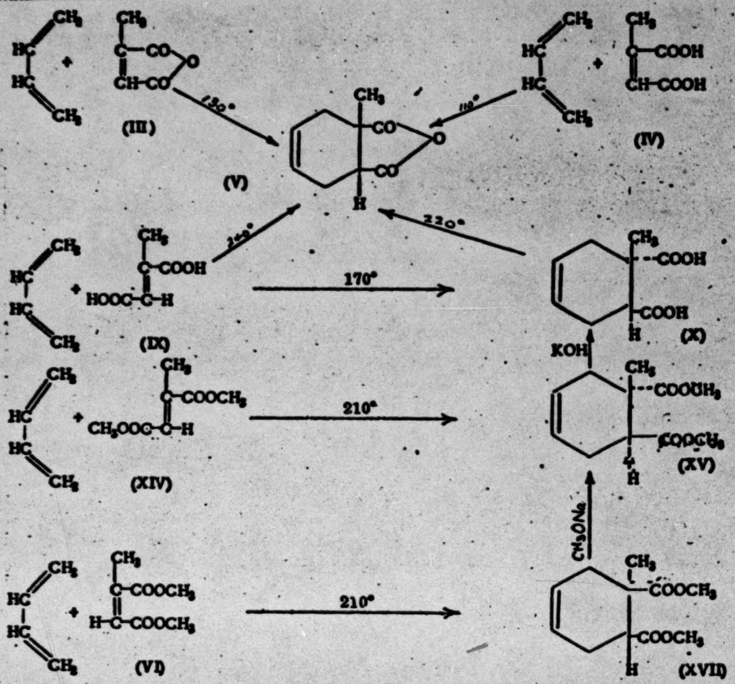
It appeared to us that the problem might be solved by the application of methods of diene synthesis, starting with the appropriate transdienophils such as mesaconic acid and its esters. In spite of the great number of papers published on the diene synthesis, we know of only a few examples of the use of trans-dienophils in reactions of diene condensation.

The condensation of fumaric and mesaconic acids with anthracene [5], 1-vinylnaphthalene and 6-methoxy-vinylnaphthalene [6], of fumaryl chloride with divinyl [7] and of fumaric acid with piperylene [8], and certain other cases have been described in the literature.

We began this work on the systematic study of diene condensations with trans-dienophils with the simplest cases, taking divinyl as the diene component, and studying its condensation with citraconic anhydride and citraconic or mesaconic acids and their esters.

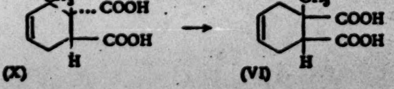
One mol of citraconic anhydride (III) is heated for 4 hrs at 130° with 3 mol of divinyl, to give the anhydride (V) of cis-1-methyl-cyclohex-4-ene-1,2-dicarboxylic acid, in 85% yield, calculated on actually reacted citraconic anhydride; this substance has already been described [9, 10]. It is hydrolyzed by boiling water, giving cis-1-methylcyclohex-4-ene-1,2-dicarboxylic acid (VI), m.p. 168° (also previously described), which when hydrogenated with Pd catalyst affords cis-1-methylcyclohexane-1,2-dicarboxylic acid (VII), which has also been described before, and which when cautiously heated with acetyl chloride yields the corresponding anhydride (VIII), m.p. 72°, also prepared by hydrogenation of the unsaturated anhydride (V) with Pd catalyst in dioxan.

The same anhydride (V) is obtained in 70% yield by heating citraconic acid (IV) with 3 mol of divinyl at 110° for 4 hrs. Mesaconic acid (IX) condenses with divinyl with much more difficulty than does citraconic acid and its anhydride. Thus when 1 mol of mesaconic acid is condensed with 8 mol of divinyl in dioxan (3 hrs at 170°) the yield of trans-1-methylcyclohex-4-ene-1,2-dicarboxylic acid (X), m.p. 180°, amounts to 40%; 40% of the mesaconic acid taken remains unchanged in the reaction mixture, and product (X) has to be separated from it by fractional crystallization.

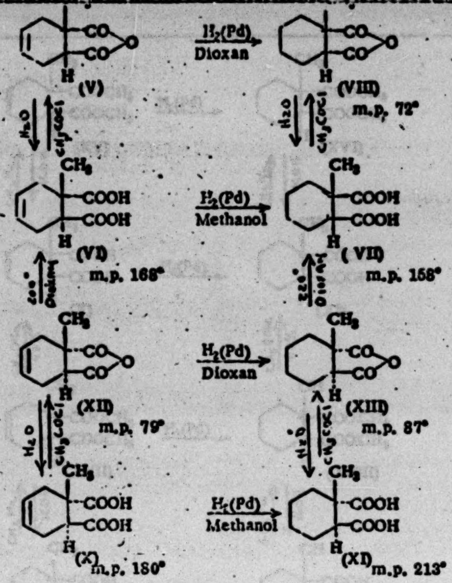

CH₃
HC
HC
CH₃
C-CO
CH-CO
O
(III)
150°
CH₃
CO
O
CO
H
(V)
110°
CH₃
C-COOH
CH-COOH
(IV)
C-COOH
HOOC-C-H
(IX)
240°
170°
220°
COOH
COOH
H
(X)
KOH
C-COOCH₃
CH₃OOC-C-H
(XIV)
210°
COOCH₃
COOCH₃
(XV)
CH₃ONa
C-COOCH₃
H-C-COOCH₃
(VI)
210°
COOCH₃
COOCH₃
(XVII)

Hydrogenation of the trans-acid (X) in methanol solution with Pd catalyst gives trans-1-methylcyclohexane-1,2-dicarboxylic acid (XI), m.p. 213-214°, which has been described in the literature [1,2,11]; trans-1-methylcyclohex-4-ene-1,2-dicarboxylic acid (X) and acetyl chloride give the corresponding unsaturated trans-anhydride (XII), m.p. 79°, hydrogenation of which (Pd catalyst) affords the anhydride of trans-1-methylcyclohexane-1,2-dicarboxylic acid (XIII), m.p. 87°, also obtained from the trans-acid (XI) by the action of acetyl chloride. The anhydrides (XII) and (XIII) are readily hydrolyzed by boiling water, giving the pure trans-acids (X) and (XI), respectively, and are converted into the corresponding cis-acids (VI) and (VII) when heated with dioxan at 200-220°, followed by hydrolysis.

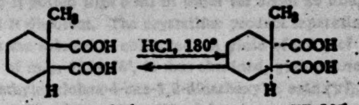
Condensation of mesaconic acid with divinyl did not take place under milder conditions (3 hr. at 110°). The chief product under more drastic conditions (4 hr. at 220-240°) is the anhydride of cis-1-methylcyclohex-4-ene-1,2-dicarboxylic acid (V), obtained in up to 50% yield. This thermal isomerization of trans- to cis-isomer established for the cases of the trans-anhydrides (XII) and (XIII) was also found for pure trans-1-methylcyclohex-4-ene-1,2-dicarboxylic acid (X), which is largely converted into the cis-isomer (VI) by heating for 3 hr. in dioxan at 200°.


CH₃
COOH
COOH
H
(X)
CH₃
COOH
COOH
H
(VI)

These findings confirm earlier observations of the greater stability of the cis-configuration of 1-methylcyclohexane-1,2-dicarboxylic acid, as compared with the corresponding non-methylated dicarboxylic acid. As has been noted by Linstead [2], cis-1-methylcyclohexane-1,2-dicarboxylic acid when treated with concentrated hydrochloric acid at 180° gives a mixture containing only about 15% of the trans-isomer, whereas cis-hexahydrophthalic acid is



quantitatively converted into the trans-isomer under these conditions. We have shown that cis- (VII) and trans-1-methylcyclohexane-1,2-dicarboxylic acid (XI) give the same equilibrium mixture, containing about 80% of cis- and 20% of trans-isomer, when heated with concentrated hydrochloric acid at 180°, suggesting the equilibrium:



(VII) 80% (XI) 20%

Dimethyl mesaconate (XIV) condenses fairly readily with divinyl. When 1 mol. of the ester (XIV) is heated for 3 hours at 210° with 5 mol. of divinyl in benzene a yield of up to 90% of the reacted ester is obtained as dimethyl trans-1-methylcyclohex-4-ene-1,2-dicarboxylate (XV), b.p. 97° /2 mm., n_D^{20} 1.4740. When hydrolyzed with 20% aqueous potassium hydroxide it gives trans-1-methylcyclohex-4-ene-1,2-dicarboxylic acid (X), and when hydrogenated (Pd catalyst in methanol) it affords dimethyl trans-1-methylcyclohexane-1,2-dicarboxylate (XVI), which when hydrolyzed with 20% caustic potash gives pure trans-1-methylcyclohexane-1,2-dicarboxylic acid (XI). The structure of the dimethyl esters (XV) and (XVI) was established by synthesizing them from the corresponding trans-acids (X) and (XI), which were methylated with diazomethane in ethereal solution.

Dimethyl citraconate does not react readily with divinyl. The reaction hardly proceeds at all at 170°, while under similar conditions as for dimethyl mesaconate (4 hr. at 210°) the product contains only 12% of condensate, the rest being unchanged ester. Hydrolysis of the condensate with 20% caustic potash gives cis-1-methylcyclohex-4-ene-1,2-dicarboxylic acid (VI) (overall yield not more than 10%). These observations are in line with the earlier one that divinyl reacts with cis-cinnamic acid much less readily than with trans-cinnamic acid [12].

Pure dimethyl cis-1-methylcyclohex-4-ene-1,2-dicarboxylate (XVII), b.p. 98°/2 mm., n_D^{20} 1.4745, was obtained from the cis-acid (VI) by methylation with diazomethane, and was hydrogenated (Pd catalyst), to afford dimethyl cis-1-methylcyclohexane-1,2-dicarboxylate (XVIII), also prepared by methylation of the cis-acid (VII) with diazomethane. (See top of next page for diagram).

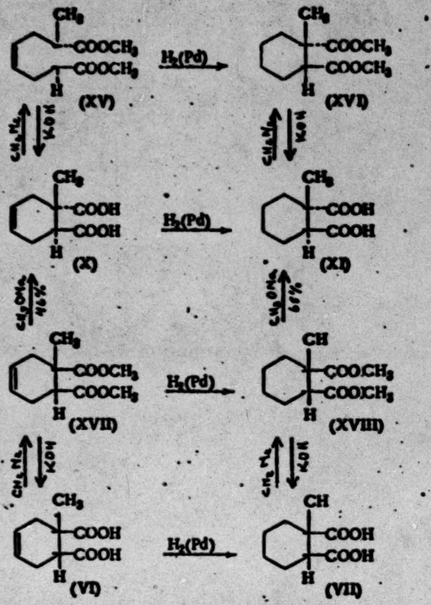
Trans-1-methylcyclohex-4-ene-1,2-dicarboxylic acid (X) is obtained in 40% yield by prolonged boiling of dimethyl cis-1-methylcyclohex-4-ene-1,2-dicarboxylate (XVII) with 15% sodium methoxide in methanol, followed by hydrolysis of the product. Under the same conditions dimethyl cis-1-methylcyclohexane-1,2-dicarboxylate (XVIII) gives up to 65% yields of trans-1-methylcyclohexane-1,2-dicarboxylic acid (XI). The degree of isomerization is much smaller under milder conditions.

EXPERIMENTAL

Citraconic acid was prepared in the usual way by the pyrolysis of citric acid [13]. Mesaconic acid was obtained by isomerization of citraconic anhydride with dilute nitric acid [14]. Dimethyl citraconate and mesaconate were prepared by esterification of the appropriate acids in the presence of sulfuric acid [15].

I. Condensation of divinyl with citraconic anhydride.

A solution of 17 g of citraconic anhydride (b.p. 103-106°/20 mm, n_D^{20} 1.4720) and 25 g of divinyl in 150 ml of dry benzene is heated in a steel cylinder for 4 hours at 130-135°. The benzene solution is separated from the solid



polymer of divinyl which forms, the benzene is distilled off, and the residue is vacuum-distilled, collecting the fraction boiling at 111-115°/4 mm., which is redistilled, to give 18.5 g of cis-1-methylcyclohex-4-ene-1,2-dicarboxylic acid (V), b.p. 113-115°/4 mm., n_D^{20} 1.4890.

Hydrolysis of the anhydride (V). 3.5 g of anhydride is boiled with 5 ml of water for about 20 min., until it dissolves. The crystalline product separating from the solution is collected. A yield of 3.8 g of acid of m.p. 165-166°, is thus obtained, giving pure cis-1-methylcyclohex-4-ene-1,2-dicarboxylic acid (VI), m.p. 168°, when recrystallized from water; the m.p. coincides with that cited in the literature [10].

Hydrogenation of the acid (VI). 1.7 g of acid (VI) is hydrogenated in methanol solution in presence of Pd catalyst, 1 mol. of hydrogen being absorbed (210 ml at 0° and 760 mm). The solvent is distilled off, leaving 1.65 g of cis-1-methylcyclohexane-1,2-dicarboxylic acid (VII), which melts at 158° after recrystallization from water. 0.4 g of this acid (VII) is heated in a sealed glass tube with 3 ml of concentrated hydrochloric acid for 7 hours at 180°; the product crystallizing out from the cooled solution melts indefinitely at 145-190°. Fractional crystallization from water and aqueous acetone gives 0.05 g of trans-1-methylcyclohexane-1,2-dicarboxylic acid (XI), m.p. 210-212°.

Cis-1-Methylcyclohexane-1,2-dicarboxylic anhydride (VIII). a) 3 g of the anhydride (V) in 15 ml of absolute dioxan is hydrogenated, over Pd catalyst, 1 mol. of hydrogen being absorbed (420 ml at 17°/750 mm). The solvent is distilled off in vacuum, leaving a liquid product, which, after repeated treatment with light petroleum, distilling off the solvent in vacuum, and cooling the residue, finally crystallizes, giving 2.9 g of a product of m.p. 69-71°, raised to 71-72° by recrystallization from light petroleum.

Found %: C 64.48; 64.63; H 7.45; 7.43. $C_9H_{12}O_3$. Calculated %: C 64.30; H 7.20.

Hydrolysis of this anhydride (VIII) by boiling with water gives a quantitative yield of cis-1-methylcyclohexane-1,2-dicarboxylic acid (VII), m.p. 157-158°.

b) 0.7 g of cis-1-methylcyclohexane-1,2-dicarboxylic acid (VII) is boiled with 3 ml of acetyl chloride on a water bath, for about 20 min., until it dissolves. The acetyl chloride is distilled off in vacuum, and the residue, which crystallizes after treatment with light petroleum, is recrystallized from light petroleum, giving 0.5 g of cis-anhydride (VIII) of m.p. 72-72.5°.

II. Condensation of Divinyl with Citraconic Acid (IV).

A solution of 6.5 g of citraconic acid (m.p. 91-93°) and 8 g of divinyl in 50 ml of anhydrous benzene, with a small amount of phenyl-2-naphthylamine, is heated for 4 hours at 110-115° in a sealed tube. The benzene solution is separated from the water formed in the reaction, and the benzene is distilled off in vacuum. The residue is a viscous oil, not crystallizing after treatment with various solvents, and after long standing. Vacuum distillation gives 5.5 g of cis-1-methylcyclohex-4-ene-1,2-dicarboxylic anhydride (V), b.p. 105-107°/2.5 mm, n_D^{20} 1.4885.

III. Condensation of Divinyl with Mesaconic Acid (IX)

a) A solution of 6.5 g of mesaconic acid (m.p. 203-205°) and 25 g of divinyl in 150 ml of dioxan is heated for 3 hours at 170-175° in a steel cylinder. The solvent is then distilled off in vacuum, the residue is treated with dry benzene, and the crystalline product is collected by filtration, giving 7.25 g of substance of m.p. 135-160°, which when recrystallized from acetone affords 4.9 g of product of m.p. 155-170°, from which a second recrystallization from acetone with a little light petroleum gives a pure product (2.1 g), of m.p. 180-182°. The residual solutes in the mother liquors are twice recrystallized from water, giving 1.7 g of substance of m.p. 160-175°, which is recrystallized from 10:1 acetone-petroleum ether mixture, giving a further 0.85 g of product of m.p. 179-181°. The total yield of condensation product is 2.05 g (35.5%) of trans-1-methylcyclohex-4-ene-1,2-dicarboxylic acid (X), m.p. 180-181°.

Found %: C 59.04; 58.91; H 6.89; 7.15. $C_9H_{12}O_4$. Calculated %: C 58.70; H 6.80.

The crystalline substance (3.8 g) remaining after separation of the acid (X) is chiefly unchanged mesaconic acid with a small admixture of the acid (X); it may be used for further condensations.

b) A mixture of 1.3 g of mesaconic acid, 5.5 g of divinyl, 25 ml of dioxan, and a small amount of phenyl-2-naphthylamine is heated for 4 hours at 240-245° in a sealed tube. The solvent is distilled off, leaving a dark-colored, viscous oil, which is soluble in benzene but does not crystallize from it or from other solvents. Vacuum distillation gives 0.7 g of cis-1-methylcyclohex-4-ene-1,2-dicarboxylic anhydride (V), b.p. 108-110°/3 mm., n_D^{23} 1.4895, which is hydrolyzed, and the product is recrystallized from water, giving 0.5 g of cis-1-methylcyclohex-4-ene-1,2-dicarboxylic acid (VI), m.p. 166-168°.

Isomerization of the trans-acid (X). 0.25 g of trans-acid (X) is heated with 3 ml of dioxan for 3 hours at 200-210°, in a sealed tube. The solvent is distilled off, and the oily residue is hydrolyzed, giving 0.2 g of crystalline product, m.p. 135-150°, recrystallization of which from a 5:1 acetone-benzene mixture gives 0.1 g of cis-1-methylcyclohex-4-ene-1,2-dicarboxylic acid (VI), m.p. 168-169°, not depressing the melting point of a sample of pure cis-acid (VI).

Hydrogenation of trans-acid (X). 0.5 g of trans-1-methylcyclohex-4-ene-1,2-dicarboxylic acid (X) in 10 ml of methanol is exhaustively hydrogenated, using Pd catalyst. The solvent is distilled off in vacuum, leaving 0.48 g of crystalline product, m.p. 208-210°, recrystallization of which from 40% aqueous acetone gives 0.35 g of trans-1-methylcyclohexane-1,2-dicarboxylic acid (XI), m.p. 212-213°, in agreement with published data [2, 11]. This acid does not depress the m.p. of a sample of trans-acid (XI) obtained by isomerization of the cis-acid (VII) with concentrated hydrochloric acid.

Found %: C 57.80; 57.70; H 7.64; 7.68. $C_9H_{14}O_4$. Calculated %: C 58.0; H 7.60.

Isomerization of the trans-acid (XI). 0.3 g of trans-acid (XI) is heated with 3 ml of concentrated hydrochloric acid for 7 hours at 190°, in a sealed tube. Fractional crystallization from water and aqueous acetone of the crystalline product obtained gave 0.03 g of the initial trans-acid (XI) and 0.1 g of cis-acid (VII), m.p. 156-158°.

Anhydride of trans-1-methylcyclohex-4-ene-1,2-dicarboxylic acid (XII). One g of trans-acid (X) is heated on a water bath with boiling acetyl chloride until it passes completely into solution (20 min.), when the excess of acetyl chloride is distilled off in vacuum. The residual oil gradually crystallizes, and after recrystallization from light petroleum gives 0.8 g of trans-anhydride (XII), m.p. 78-79°.

Found %: C 65.20; 65.31; H 6.19; 6.21. $C_9H_{10}O_3$. Calculated %: C 65.04; H 6.06.

This anhydride is hydrolyzed by boiling with water, giving the initial trans-acid (X) in quantitative yield (m.p. 180-181°).

Isomerization of the trans-anhydride (XII). 0.2 g of trans-anhydride (XII) are heated for 2 hours at 190-200° with 3 ml of dioxan, in a steel cylinder. The liquid residue remaining after distilling off the dioxan is hydrolyzed by boiling with water, and the resulting cis-acid (VI) is twice recrystallized from water, giving 0.08 g of product melting at 165-167°.

Trans-1-Methylcyclohexane-1,2-dicarboxylic anhydride (XIII). a) 0.5 g of trans-acid (XI) and 3 ml of acetyl chloride are heated at the b.p. to complete dissolution, and the acetyl chloride is then distilled off in vacuum. The residual oily product gradully crystallizes when treated with light petroleum, after recrystallization from which 0.35 g of trans-anhydride (XIII), m.p. 87-88°, is obtained.

Found %: C 64.36; 64.48; H 7.29; 7.33. $C_9H_{12}O_3$. Calculated %: C 64.30; H 7.20.

The initial trans-acid (XI), m.p. 212-213°, is obtained quantitatively by hydrolyzing the anhydride (XIII) with water.

b) 0.4 g of trans-1-methylcyclohex-4-ene-1,2-dicarboxylic anhydride (XII) in 5 ml of absolute dioxan is hydrogenated, using Pd catalyst. The liquid residue remaining after distilling off the solvent in vacuum is recrystallized from light petroleum, giving 0.3 g of anhydride (XIII), m.p. 87-88°.

Isomerization of the trans-anhydride (XIII). 0.3 g of the trans-anhydride (XIII) is heated with 4 ml of dioxan in a sealed tube for 2 hours at 200-210°. The liquid residue remaining after distilling off the dioxan is hydrolyzed by boiling with water, and the product is twice recrystallized from water, giving 0.2 g of pure cis-acid (VII), m.p. 157-158°.

IV. Condensation of divinyl with dimethyl mesaconate (XIV).

A mixture of 9.2 g of dimethyl mesaconate (b.p. 90-91°/12 mm, n_D^{20} 1.4460), 16.5 g of divinyl, and 40 ml of dry benzene is heated for 3 hours at 210-215° in a steel cylinder. The solvent is distilled off, and the residue is fractionated in vacuum:

Fraction 1, b.p. 65-95°/3 mm., n_D^{20} 1.4650; weight 2.2 g.
Fraction 2, b.p. 99-102°/3 mm., n_D^{20} 1.4735; weight 8.5 g.

A large amount of divinyl polymer remains in the flask. A second fractional distillation gives 1.8 g of the initial dimethyl mesaconate (n_D^{20} 1.4480) and 8.7 g of dimethyl trans-1-methylcyclohex-4-ene-1,2-dicarboxylate (XV), yield 87% calculated on reacted mesaconic ester, b.p. 97°/2 mm, n_D^{20} 1.4742, d_4^{20} 1.1170; MR_D found 53.41, calculated 53.64.

Found %: C 62.25; 62.19; H 7.62; 7.79. $C_{11}H_{16}O_4$. Calculated %: C 62.50; H 7.60.

The trans-diester (XV) was also obtained from trans-1-methylcyclohex-4-ene-1,2-dicarboxylic acid (X) and diazomethane in ethereal solution; it had the same constants (b.p. 97°/2 mm., n_D^{20} 1.4738).

Hydrolysis of the trans-diester (XV). 3.2 g of trans-diester (XV) is boiled with 20 ml of 20% aqueous caustic potash until it dissolves (about 20 min.). The light yellow solution is filtered through active charcoal, and concentrated hydrochloric acid is added to the filtrate until it becomes acid to Congo red. 2.6 g of acid of m.p. 179-181°, not depressing the m.p. of a sample of pure trans-acid (X), is obtained.

Hydrogenation of trans-ester (XV). 3.2 g of dimethyl trans-1-methyl-cyclohex-4-ene-1,2-dicarboxylate (XV) in 20 ml of methanol is hydrogenated, using Pd catalyst. One mol. of hydrogen was absorbed (335 ml at 0° and 760 mm). The methanol was distilled off, and the residue was fractionally distilled in vacuum, giving 3 g of dimethyl trans-1-methyl-cyclohexane-1,2-dicarboxylate (XVI), b.p. 95°/2 mm., n_D^{20} 1.4639, d_4^{20} 1.0940; MR_D Found 53.95, Calculated 54.11.

Found %: C 61.57; 61.39; H 8.60; 8.63. $C_{11}H_{18}O_4$. Calculated %: C 61.60; H 8.45.

The same ester (XVI), b.p. 95°/2 mm., n_D^{20} 1.4636, was obtained in theoretical yield by the action of diazomethane on the trans-acid (XI) in ethereal solution.

The trans-ester (XVI) (0.5 g) is boiled with 5 ml of 20% aqueous caustic potash until it goes into solution, the solution is filtered through active charcoal, the filtrate is made acid to Congo red, and the precipitate forming is collected, and recrystallized from 50% aqueous acetone, giving 0.35 g of trans-1-methylcyclohexane-1,2-dicarboxylic acid (XI), m.p. 211-213°, not depressing the m.p. of a sample of pure trans-acid (XI).

V. Condensation of divinyl with dimethyl citraconate.

A mixture of 9.8 g of dimethyl citraconate (b.p. 96-97°/12 mm; n_D^{20} 1.4470) and 17 g of divinyl in 40 ml of dry benzene is heated in a steel cylinder for 3 hours at 210-215°. The residue after distilling off the solvent is extracted with acetone, in order to separate the product from divinyl polymer, the acetone is distilled off, and the residue is fractionally distilled in vacuum.

Fraction 1, wt. 6.1 g., b.p. 99-109°/15 mm; n_D^{20} 1.4550.
Fraction 2, wt. 2.5 g., b.p. 110-130°/15 mm; n_D^{21} 1.4700.

Redistillation of Fraction 1 gave 5.6 g of pure dimethyl citraconate (b.p. 97°/12 mm; n_D^{20} 1.4490). Repeated fractionation of Fraction 2 gave 1.6 g of condensation product, b.p. 97-100°/2 mm; n_D^{20} 1.4715, hydrolysis of which with 20% aqueous caustic potash gives cis-1-methyl-cyclohex-4-ene-1,2-dicarboxylic acid (VI), m.p. 167-168°, yield after recrystallization 1.2 g., or 10-12% of theoretical.

VI. Preparation of dimethyl cis-1-methylcyclohex-4-ene-1,2-dicarboxylate (XVII), and its isomerization.

A slight excess of diazomethane in ether is added gradually to a suspension of 6 g of cis-1-methylcyclohex-4-ene-1,2-dicarboxylic acid (VI) in 40 ml of absolute ether, the ether is distilled off, and the residue is fractionally distilled in vacuum, giving 6.5 g of dimethyl ester (XVII), b.p. 98°/2 mm; n_D^{20} 1.4745; d_4^{20} 1.1210; MR_D

found 53.28, calculated 53.64.

Found %: C 62.41; 62.26; H 7.64; 7.77. $C_{11}H_{16}O_4$. Calculated %: C 62.50; H 7.60.

Hydrolysis of the dimethyl ester (XVII) with 20% aqueous caustic potash regenerates the initial cis-acid (VI), in theoretical yield.

Isomerization of the cis-ester (XVII). A mixture of 4.5 g of cis-ester (XVII) and sodium methoxide (12 g of sodium dissolved in 300 ml of absolute methanol) in methanol is boiled on a water bath for 12 hours. The methanol is distilled off in vacuum, the residue is dissolved in a small volume of water, the solution is extracted with ether, and the aqueous layer is evaporated down to small volume in a porcelain bowl on a water bath. The deposit of sodium salts forming is filtered off and dissolved in 20 ml of water, 60% sulfuric acid is added to an acid reaction to Congo red, and the crystalline precipitate forming is collected; yield, 2.5 g of acid of m.p. 168-175°, or, after crystallization from 10:1 acetone-light petroleum mixture, 1.8 g (46% of theoretical) of trans-1-methylcyclohex-4-ene-1,2-dicarboxylic acid (X), m.p. 179-181°, not depressing the m.p. of a sample of known pure acid.

VII. Preparation of dimethyl cis-1-methylcyclohexane-1,2-dicarboxylate (XVIII), and its isomerization.

Similarly to the preceding experiment, 4.8 g of cis-1-methylcyclohexane-1,2-dicarboxylic acid (VII) and diazomethane in ether gave 5.1 g of pure cis-ester (XVIII), b.p. 95°/2 mm, n_D^{20} 1.4635, d_4^{20} 1.0935; MR_D found 54.01, calculated 54.11.

Found %: C 61.35; 61.25; H 8.48; 8.37. $C_{11}H_{18}O_4$. Calculated %: C 61.60; H 8.45.

The dimethyl ester (XVIII) is also obtained in theoretical yield by hydrogenation of dimethyl cis-1-methylcyclohex-4-ene-1,2-dicarboxylate (XVII) in methanol solution, using Pd catalyst. Hydrolysis of the ester with 20% aqueous caustic potash gives the cis-acid (VII) in theoretical yield.

Isomerization of the cis-ester (XVIII). 4.1 g of cis-ester (XVIII) is boiled for 12 hours on a water bath with a solution of sodium methoxide prepared from 10 g of sodium and 250 ml of absolute methanol. The solution is evaporated to dryness in vacuum, the residue is dissolved in a small volume of water, and the solution is extracted with ether. The aqueous solution is evaporated down to small volume in a porcelain basin on a water bath, the deposit of sodium salts is collected, and dissolved in 15 ml of water, which is filtered through active charcoal, and the filtrate is made acid to Congo red with concentrated hydrochloric acid, giving 2.75 g of acid of m.p. 197-205°, which when recrystallized from 60% aqueous acetone gives 2.3 g (65% of theoretical) of pure trans-1-methylcyclohexane-1,2-dicarboxylic acid (XI), m.p. 212-213°, not depressing the m.p. of a known sample of the acid.

SUMMARY

1. Condensation of divinyl with citraconic anhydride, citraconic acid, mesaconic acid, and their dimethyl esters gives the cis- and trans-1-methyl-cyclohexane-1,2-dicarboxylic acids (VI), (VII), (X), and (XI), their anhydrides (V), (VIII), (XII), and (XIII), and their dimethyl esters (XV), (XVI), (XVII), and (XVIII).

2. Condensation of divinyl with dimethyl mesaconate gives dimethyl trans-1-methylcyclohex-4-ene-1,2-dicarboxylate (XV) in good yield; the trans-acids (X), and (XI) are readily hence derived.

3. The dimethyl esters of the cis-acids (XVII) and (XVIII) are converted by the action of sodium methoxide into the corresponding trans-acids (X) and (XI), in good yield.

4. The trans-acids (X) and (XI), and their anhydrides (XII) and (XIII) isomerize when heated at 200°, to afford the corresponding cis-compounds.

LITERATURE CITED

[1] W. Bachmann, S. Kushner, J. Am. Chem. Soc. 65, 1963 (1943). [2]* R. Linstead, A. Millidge, J. Chem. Soc., 478 (1936). [3] R. Linstead, A. Millidge, A. Walpale, J. Chem. Soc. 1140 (1937). [4] W. Johnson, J. Am. Chem. Soc. 66, 216 (1944). [5] W. Bachmann, L. Scott, J. Am. Chem. Soc. 70, 1458 (1948). [6] W. Bachmann, L. Scott, J. Am. Chem. Soc. 70, 1462 (1948). [7] K. Alder, M. Schumacher, . Ann. 565, 96 (1949). [8] D. Craig, J. Am. Chem. Soc. 72, 1678 (1950). [9] I.N. Nazarov and L.N. Pinkina, J. Gen. Chem. 20, 2009 (1950).* [10] F. Vocke, . Ann. 497, 247 (1932). [11] P. Mukharje, J. Ind. Chem. Soc. 25, 365 (1948). [12] K. Alder, H. Vagt, H. Vogt, . Ann. 565, 135 (1949). [13] Syntheses of Organic Compounds, II, GIIL 570 (1949). [14] Ibid. II, GIIL 312 (1949). [15] G. Jeffery, A. Vogel, J. Chem. Soc., 654, (1948).

Received November 20, 1951

Institute of Organic Chemistry, Academy of Sciences U.S.S.R.

---

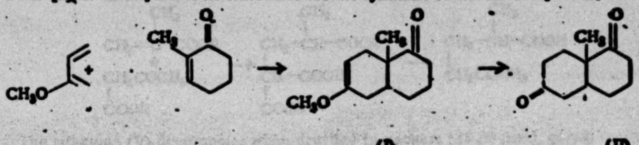
* See Consultants Bureau translation, p. 2079.

BLANK
PAGE

SYNTHESIS OF STEROID COMPOUNDS AND OF RELATED SUBSTANCES. XII. CONDENSATION OF CYCLIC β-DIKETONES WITH VINYL KETONES, AND TRANSFORMATIONS OF THE RESULTING PRODUCTS

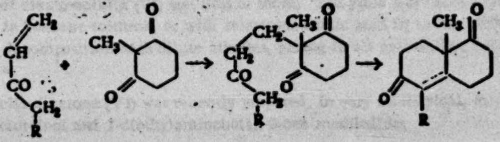
I. N. Nazarov and S. I. Zavyalov

Methoxy-octalone (I), prepared in our laboratory by the condensation of 2-methoxybutadiene with 1-methylcyclohex-1-ene [1], is an important intermediate for the synthesis of steroid compounds:

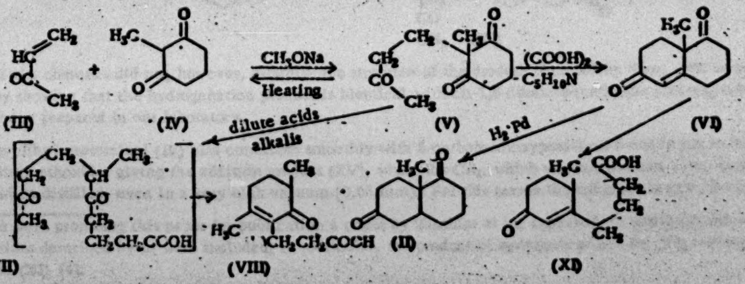

(I) (II)

Hydrolysis of methoxyoctalone (I) with dilute acids gives diketomethyldecalin (II). Since the above ketones (I) and (II) were obtained by the method of diene condensation they must belong to the cis-decalin series, so that they can be used for the synthesis of only such steroid systems as have the cis-configuration of rings A and B. However, most of the biologically important steroids, in particular the steroid hormones, have the A-B and C-D rings joined in the trans-position. Many important steroid hormones (progesterone, testosterone, corticosterone, cortisone, etc.) have a double bond at C_4-C_5 in the ring system A-B. For these reasons we thought it necessary to work out convenient methods for the preparation of 1,6-diketo-9-methyl-Δ^5-octalin (VI), as a starting substance for the synthesis of these steroid hormones and of other related substances.

With this end in view we decided to begin our studies with the reaction of condensation of vinyl ketones with methyldihydroresorcinol, with cyclization of the resulting product, according to the scheme:

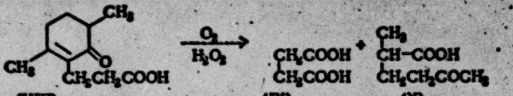


Methyldihydroresorcinol (IV) condenses with vinyl methyl ketone (III) in the presence of sodium methoxide in methanol, to give the triketone (V) in 60-65% yield, together with a small amount of the cyclic ketoacid (VIII), formed as a result of hydrolytic fission of the triketone (V), followed by cyclization of the diketo-acid (VII), arising as an intermediate product.

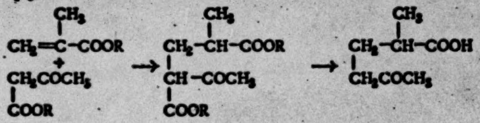


(III) (IV) (V) (VI) (VII) (VIII) (II) (XI)

The triketone (V) was in fact found to be very readily hydrolyzable, both by dilute acids and alkalis at room temperature, with opening of the dihydroresorcinol cycle, giving the intermediate product (VII), which undergoes ring closure with production of the unsaturated keto-acid (VIII), the structure of which was established from a study of its ozonation products, viz., succinic acid (IX) and hexan-5-one-2-carboxylic acid (X):

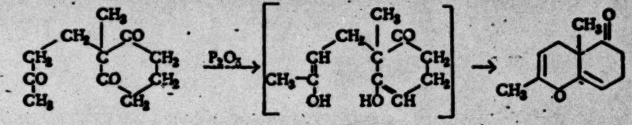

(VIII) (IX) (X)

The latter acid was also synthesized from acetoacetic and methacrylic esters, which were condensed, the product was hydrolyzed, and the hexan-2-one-3,5-dicarboxylic acid so obtained was decarboxylated, giving hexan-5-one-2-carboxylic acid [2]:



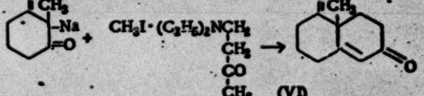
$$CH_2{=}C(CH_3){-}COOR + CH_3COCH_2COOR \rightarrow CH_2{-}CH(CH_3){-}COOR,\ CH(COOR){-}COCH_3 \rightarrow CH_2{-}CH(CH_3){-}COOH,\ CH_2COCH_3$$

The triketone (V) decomposes when distilled in vacuum (15-20 mm), giving methyldihydroresorcinol. When heated with phosphorus pentoxide it affords chromanone (XII) in high yield:


(V) (XII)

The extraordinary ease of hydrolysis of the triketone (V), with its conversion into the keto-acid (VIII), was the chief obstacle in realizing cyclization of triketone (V) into diketo-octalin (VI). This important reaction was studied in the greatest detail, the best results being obtained when the triketone (V) was heated with salts of secondary amines, when the yield of diketo-octalin (VI) was 60% or more. The yield was much lower when the triketone (V) was heated with piperidine in benzene solution, or with anhydrous oxalic acid in vacuo. Diketo-octalin (VI) itself readily undergoes hydrolytic decomposition with dilute alkalies, giving in all probability, the unsaturated keto-acid (VIII) or other isomeric acids.*

The bicyclic diketone (VI) was recently prepared, in very small yield, by Wieland and Miescher [3], from methyldihydroresorcinol and 1-diethylaminobutan-3-one methiodide:


(VI)

The Swiss chemists did not, however, establish the structure of the product obtained by them. We were able to do this by showing that the hydrogenation product is identical with cis-1,6-diketo-9-methyldecalin (II), which had previously been prepared in our laboratory.

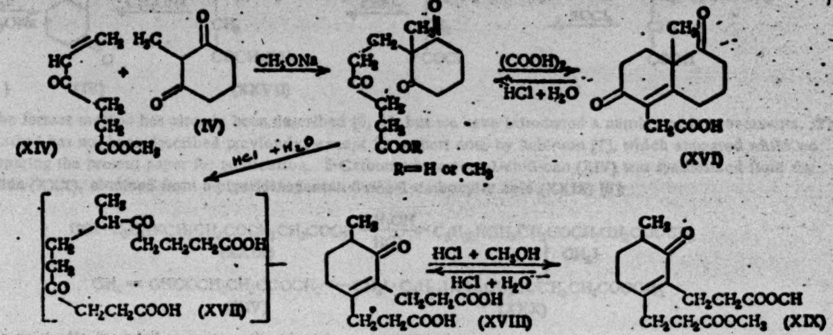
Methyldihydroresorcinol (IV) also condenses smoothly with 5-carbomethoxypent-1-en-3-one (XIV) in the presence of sodium ethoxide, giving the addition product (XV), where R=CH_3, which was not isolated pure, since it decomposed when distilled, even in a very high vacuum (0.05 mm). For this reason the triketoester (XV, R=CH_3)

---

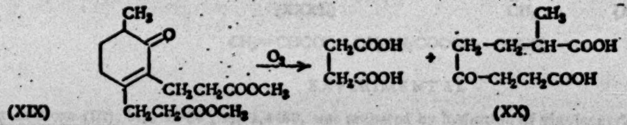
* While we were preparing this paper for publication a paper by Tischler et al. appeared, in which certain of the transformations described by us were included; in particular, the product of hydrolysis of octalin (VI) is assigned the structure (XI) [4]:

was subjected to cyclization without previous purification, by heating in vacuum with anhydrous oxalic acid, when crystalline 1,6-diketo-5-carboxymethyl-9-methyl-Δ^5-octalin (XVI) is obtained in good yield.

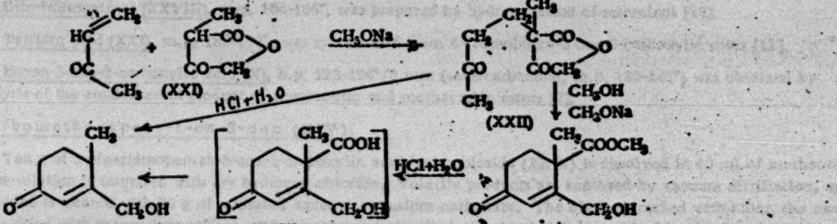
When heated with hydrochloric acid the triketoester (XV, R = CH_3) changes fairly readily into the unsaturated cyclic keto-dicarboxylic acid (XVIII), by the above-described process of hydrolytic fission of the dihydroresorcinol cycle, with subsequent cyclization of the intermediate product, diketocarboxylic acid (XVII). The reaction of cyclization of the triketoester of dihydroresorcinol (XV, R = CH_3) was found to be reversible, as the diketo-octalin derivative (XVI) is readily converted by heating with hydrochloric acid into the keto-dicarboxylic acid (XVIII), by hydrolytic fission, through the intermediate compounds (XV, R = CH_3) and (XVII). In the same way the diketo-octalin derivative (XVI) is converted in practically quantitative yield into the dimethyl ester (XIX) when treated with a solution of hydrogen chloride in anhydrous methanol.



Hydrolysis of the dimethyl ester (XIX) with dilute hydrochloric acid gives the ketodicarboxylic acid (XVIII), the structure of which was established, as in the preceding case, by identification of the ozonation products, succinic acid and heptan-3-one-1,6-dicarboxylic acid (XX):



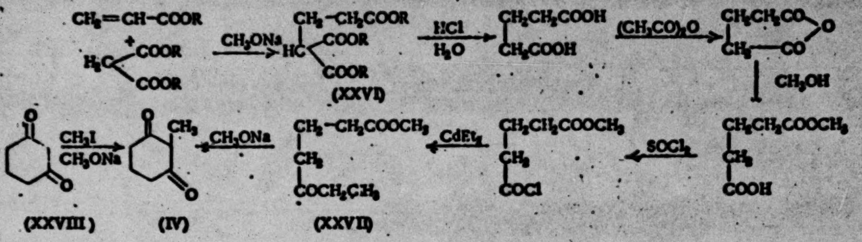
Condensation of but-1-en-3-one with the acid (XXI) in presence of sodium methoxide gives the diketolactone (XXII), in good yield:



The diketolactone (XXII) undergoes cyclization under the influence of sodium methoxide in methanol, with simultaneous opening of the lactone ring, giving the ketohydroxy-ester (XXIII). The keto-alcohol (XXV) is also formed, as a result of a process of consecutive hydrolysis and decarboxylation of the ester (XXIII). As was expected, the compounds (XXII) and (XXIII) readily afford the keto-alcohol (XXV) when boiled with hydrochloric acid.

The starting substances for the above-described reactions were prepared as follows: methyldihydroresorcinol

(IV) was obtained in two ways: 1) from acrylic ester through glutaric acid and methyl hexan-3-one-6-carboxylate (XXVII), and 2) by methylation of dihydroresorcinol (XXVIII):

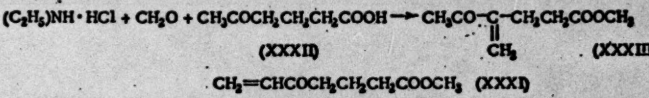


The former method has already been described [5, 6], but we have introduced a number of improvements. The latter method has not been described previously, except for a short note by Robinson [7], which appeared while we were preparing the present paper for publication. 5-Carbomethoxypent-1-en-3-one (XIV) was synthesized from the methiodide (XXX), obtained from 5-piperidinopentan-3-one-1-carboxylic acid (XXIX) [8]:

$$\underset{(XXIX)}{HCl\cdot C_5H_{10}NCH_2CH_2COCH_2CH_2COOH} \xrightarrow[HCl]{CH_3OH} C_5H_{10}NCH_2CH_2COCH_2CH_2COOCH_3 \;\downarrow CH_3I$$

$$\underset{(XIV)}{CH_2=CHCOCH_2CH_2COOCH_3} \leftarrow \underset{(XXX)}{CH_3I\cdot C_5H_{10}NCH_2CH_2COCH_2CH_2COOCH_3}$$

We originally intended to prepare the vinyl ketone (XXXI) from pentan-4-one-1-carboxylic acid (XXXII); the Mannich reaction took place with participation of the methylene group, giving the isomeric vinyl ketone (XXXIII):



$$(C_2H_5)NH\cdot HCl + CH_2O + \underset{(XXXII)}{CH_3COCH_2CH_2CH_2COOH} \longrightarrow \underset{(XXXIII)}{CH_3CO\!-\!\underset{\overset{\|}{CH_2}}{C}\!-\!CH_2CH_2COOCH_3}$$

$$CH_2=CHCOCH_2CH_2CH_2COOCH_3 \quad (XXXI)$$

EXPERIMENTAL

But-en-3-one (III), b.p. 79-80°, n_D^{20} 1.4460, was prepared by hydration of vinylacetylene [9].

5-Piperidinopentan-3-one-1-carboxylic acid (XXIX), m.p. 145-146°, was prepared by the reaction of levulinic acid with piperidine hydrochloride and paraldehyde [8].

Dihydroresorcinol (XXVIII), m.p. 104-105°, was prepared by hydrogenation of resorcinol [10].

Tetrinic acid (XXI), m.p. 189-190°, was synthesized from 4-bromobutan-3-one-2-carboxylic ester [11].

Hexan-5-one-2-carboxylic acid (X), b.p. 123-126°/3 mm (semicarbazone, m.p. 140-141°) was obtained by hydrolysis of the condensation product of acetoacetic and methacrylic esters [2].

5-Carbomethoxypent-1-en-3-one (XIV).

Ten g of 5-piperidinopentan-3-one-1-carboxylic acid hydrochloride (XXIX) is dissolved in 40 ml of methanol, and the solution is saturated with dry hydrogen chloride. Volatile products are removed by vacuum distillation, and the residue is treated with 20 g of saturated aqueous potassium carbonate. The oil is extracted with ether, the extract is dried with magnesium sulfate, and the solvent is distilled off. Methyl iodide (15 g) is added to the residue, and the methiodide so obtained is distilled in vacuum, when it decomposes with formation of 5-carbomethoxypent-1-en-3-one (XIV), b.p. 99-100°/15 mm, n_D^{20} 1.4491; yield 3.2 g.

Found %: C 58.82; 58.62; H 7.30; 7.02. $C_7H_{10}O_3$. Calculated %: C 59.1; H 7.0.

Condensation of acetoacetic ester with methyl acrylate.

A solution of 24 g of methyl acrylate in 36 g of acetoacetic ester is added with stirring during 5 min. to a solution of sodioacetoacetic ester, prepared from 0.5 g of sodium and 36 g of acetoacetic ester. The temperature of the mixture rises after 1-2 min., and continues to do so for 2 hours, after which it is heated on a water bath at 70-80° for

90 min., when 30 ml of 1:1 hydrochloric acid is added. The oily layer which separates is dried with magnesium sulfate, and distilled; yield 46 g of 5-carbomethoxy-3-carboethoxypentan-2-one, b.p. 142-144°/10 mm [12].

Pentan-4-one-1-carboxylic acid (XXXII).

A mixture of 46 g of 5-carbomethoxy-3-carboethoxypentan-2-one and 200 ml of 1:1 hydrochloric acid is boiled under reflux for 5 hours, the hydrochloric acid layer is separated, and the residue is distilled in vacuum, giving 20 g of pentan-4-one-1-carboxylic acid (XXXII), b.p. 142-144°/10 mm [13].

Methyl 3-methylenopentan-4-one-1-carboxylate (XXXIII).

A mixture of 10 g of pentan-4-one-1-carboxylic acid, 8.5 g of diethylamine hydrochloride, and 2.5 g of paraformaldehyde was heated for 40 min. at 110-115° at 10 mm pressure, after which it is dissolved in 50 ml of dry methanol, and the solution is saturated with hydrogen chloride. The solvent is then distilled off, and the residue is treated with 10 ml of saturated aqueous potassium carbonate. The oil separating is dissolved in ether, the solution is dried with magnesium sulfate, the solvent is distilled off, and the residue is vacuum distilled, giving 4.5 g of methyl 3-methylenopentan-4-one-1-carboxylate (XXXIII), b.p. 77-81°/3 mm., n_D^{20} 1.4510.

Found %: C 61.31; 61.54; H 7.77; 7.98. $C_8H_{12}O_3$. Calculated %: C 61.54; H 7.69.

Oxidation of methyl 3-methylenopentan-4-one-1-carboxylate (XXXIII).

Two g of methyl 3-methylenopentan-4-one-1-carboxylate is heated to 90° with 20 ml of 20% nitric acid, when the solution begins to boil, with evolution of oxides of nitrogen. It is kept at the boil for 2 hours, and then evaporated to dryness in vacuum. The crystalline residue is succinic acid (0.7 g), m.p. 182-183° after recrystallization from benzene.

Preparation of propane-1,1,3-tricarboxylic ester (XXVI).

A solution of 120 g of methyl acrylate in 120 g of malonic ester is added drop by drop, during 90 min., with constant stirring, to a solution of sodiomalonic ester, prepared from 0.5 g of sodium and 240 g of malonic ester; the reaction flask is cooled, so as to maintain the temperature of the reaction mixture at 38-40°. The system is allowed to stand for 12 hours, and the product is washed with 100 ml of 1:10 hydrochloric acid, dried with magnesium sulfate, and distilled in vacuum, giving 266 g of propane-1,1,3-tricarboxylic ester (XXVI), b.p. 145-148°/14 mm [14]; 180 g of unreacted malonic ester is recovered.

Preparation of glutaric acid.

A mixture of 250 g of propane-1,1,3-tricarboxylic ester and 1.5 liters of 1:1 hydrochloric acid is boiled under reflux for 6 hours, the hydrochloric acid is distilled off in vacuum, and the residue is fractionally distilled, giving 110 g of glutaric acid, b.p. 165-170°/4 mm, m.p. 95-96° [12].

Preparation of glutaric anhydride.

A mixture of 110 g of glutaric acid and 250 ml of acetic anhydride is boiled under reflux for 2 hours, acetic anhydride and acetic acid are distilled off under reduced pressure, and 250 ml of fresh acetic anhydride is added to the residue, which is boiled for a further 2 hours under reflux. Excess of acetic anhydride and acetic acid are distilled off in vacuum, and the residue is fractionally distilled, giving 80 g of glutaric anhydride, b.p. 148-150°/12 mm, m.p. 56-57° [5].

Monomethyl glutarate.

A mixture of 80 g of glutaric anhydride and 45 g of anhydrous methanol is boiled under reflux for 1 hour, excess of methanol is distilled off, and the residue is vacuum distilled, giving 62 g of monomethyl glutartate, b.p. 140-142°/10 mm [5].

Chloride of 3-carbomethoxybutyric acid.

A mixture of 62 g of monomethyl glutarate and 150 g of thionyl chloride is heated on the water bath at 50-60° until evolution of hydrogen chloride ceases (2 hr.), when excess of thionyl chloride is distilled off, and the residue is distilled in vacuum, giving 60 g of 3-carbomethoxybutyryl chloride, b.p. 92-93°/9 mm [5].

Methyl hexan-3-one-6-carboxylate (XXVII).

22 g of finely powdered cadmium chloride is added during 8 minutes, with constant stirring, and cooling in

ice, to a Grignard reagent prepared from 5 g of magnesium, 30 g of ethyl bromide, and 80 ml of absolute ether. Stirring is continued at room temperature for 1 hour, after which 40 ml of ether are distilled off, and 80 ml of dry benzene is added to the residue. A solution of 24 g of 3-carbomethoxybutyryl chloride in 20 ml of dry benzene is added to the suspention so obtained, during 20 min., and with energetic stirring, after which it is heated on a boiling water bath for 1 hour with stirring. 30 g of ice and 50 ml of 10% hydrochloric acid are then added, the ether-benzene layer is separated, and the aqueous layer is extracted with benzene. The combined extracts are dried with magnesium sulfate, the solvents are distilled off, and the residue is fractionally distilled in vacuum, giving 19 g of methyl hexan-3-one-6-carboxylate (XXVII), b.p. 97-98°/10 mm, n_D^{20} 1.4303 [5].

Preparation of 2-methyldihydroresorcinol (IV).

a) 2.4 g of methyl hexan-3-one-6-carboxylate (XXVII) is added during 2 min. with constant stirring to a suspension of sodium methoxide, prepared from 0.7 g of sodium and 0.9 g of absolute methanol in 30 ml of absolute ether. The precipitate formed is collected after 2 hours, washed with ether, treated with 10 ml of 1:1 hydrochloric acid, and washed with water. Recrystallization from methanol gives 1.7 g of 2-methyldihydroresorcinol (IV), m.p. 208-209° [5].

b) 11.2 g of dihydroresorcinol, followed by 16 g of methyl iodide, are added to a solution of sodium methoxide, prepared from 2.3 g of sodium and 35 ml of anhydrous methanol, and the mixture is boiled on the water bath for 1 hour, after which methanol is distilled off in vacuum, and 10 ml of water is added to the residue. The crystalline precipitate formed is collected, washed with water, and recrystallized from methanol, giving 5 g of 2-methyldihydroresorcinol, m.p. 209-210°, not depressing the m.p. of the above product.

c) 2 g of dihydroresorcinol, followed by 3 g of methyl iodide, are added to a solution of 1 g of potassium hydroxide in 7 ml of anhydrous methanol, and the mixture is boiled for 40 min., after which the operations described in (b) above are performed, giving 0.4 g of 2-methyldihydroresorcinol, m.p. 209-210°, not depressing the m.p. of a known sample.

Condensation of 2-methyldihydroresorcinol (IV) with but-1-en-3-one (III).

A solution of sodium methoxide, prepared from 0.1 g of sodium and 30 ml of absolute methanol, is heated on a water bath with 3 g of 2-methyldihydroresorcinol until the latter is all dissolved, when 2 g of but-1-en-3-one is rapidly added, and heating is continued at 55-60° for 4 hours, after which the solution is made neutral by addition of concentrated hydrochloric acid, cooling with ice. The solvent is distilled off, and the residue is treated with 3 ml of water; unreacted 2-methyldihydroresorcinol (0.2 g) is filtered off, and 3 ml of saturated aqueous sodium carbonate are added to the filtrate. The oily product is extracted with ether, and the ethereal solution is dried with magnesium sulfate. The ether is then distilled off, and the residue is vacuum distilled, giving 2 g of the triketone (V), b.p. 118-125°/0.1 mm., n_D^{20} 1.4910.

Found %: C 66.92; 67.04; H 8.30; 8.51; $C_{11}H_{16}O_3$. Calculated %: C 67.31; H 8.17.

The alkaline solution remaining after ether extraction is made acid to Congo red with concentrated hydrochloric acid, the oil separating is extracted with ether, the extract is dried with magnesium sulfate, and the ether is distilled off; the crystalline residue is recrystallized from ether, giving 0.05 g of keto-acid (VIII), m.p. 48-49°.

Found %: C 67.06; 67.05; H 8.57; 8.32. $C_{11}H_{16}O_3$. Calculated %: C 67.31; H 8.17.

Equivalent found by titration 194. $C_{11}H_{16}O_3$. Calculated equivalent 196.

The substance gives no coloration with $FeCl_3$. Its semicarbazone melts at 205-208°, with decomposition.

Found %: N 17.24; 16.97. $C_{12}H_{19}O_3N_3$. Calculated %: N 16.7.

Ozonation of the keto-acid (VIII).

Oxygen containing 6% of ozone is passed for 4 hours into a solution of 2 g of the unsaturated keto-acid (VIII) in 20 ml of dry chloroform, and 20 ml of 5% perhydrol is then added, after which the mixture is boiled with vigorous stirring for 12 hours. The chloroform and water are then distilled off in vacuum, leaving a crystalline residue, from which 0.7 g of succinic acid, m.p. 182-183° (recrystallized from benzene), and 0.2 g of hexan-2-one-5-carboxylic acid semicarbazone, m.p. 140-141° (from methanol), not depressing the m.p. of known specimens of the compounds, are obtained.

Attempts at cyclization of the triketone (V).

Experiment 1. 1 g of triketone (V) was dissolved in 2 ml of concentrated sulfuric acid, cooling with ice. After standing for 2 hour at room temperature the solution was poured on ice, and the resulting solution was extracted with benzene. The benzene extract was dried with magnesium sulfate, the solvent was distilled off, and the residue was recrystallized from ether, giving the unsaturated keto-acid (VIII), m.p. 48-49°.

Experiment 2. A mixture of 2 g of triketone (V) and 1 g of oxalic acid was heated at 110-115° for 1 hour, under reflux, the product was treated with 2 g of saturated sodium carbonate solution, and extracted with benzene. The benzene was distilled off, leaving 0.2 g of a thick oil, from which a semicarbazone, m.p. 238-241°, was obtained, not depressing the m.p. of a specimen of the semicarbazone of octalin (VI). The alkaline solution remaining after benzene extraction was made acid to Congo red with concentrated hydrochloric acid, and extracted with benzene. The solvent was distilled off, leaving a crystalline residue, recrystallization of which from ether gave 1 g of the unsaturated keto-acid (VIII), m.p. 48-49°.

Experiment 3. A solution of 0.2 g of sodium hydroxide in 5 ml of water was added to 1 g of triketone (V) dissolved in 5 ml of methanol, the mixture was allowed to stand for 1 hour at room temperature, and then made acid to Congo red with concentrated hydrochloric acid, and extracted with benzene. The solvent was distilled off from the extract, and the residue was recrystallized from ether, giving 0.5 g of unsaturated keto-acid (VIII), m.p. 48-49°.

Experiment 4. 2 g of triketone (V) was added to a solution of sodium methoxide prepared from 0.1 g of sodium and 8 ml of methanol, the solution was made neutral with concentrated hydrochloric acid after 24 hour at room temperature, 0.5 g of sodium carbonate was added, and the solution was extracted with benzene. The solvent was distilled off, and the residue was fractionally distilled, giving 1 g of product of b.p. 132-138°/2 mm, n_D^{29} 1.5070, from which 0.3 g of a semicarbazone, m.p. 239-242°, was obtained, not depressing the m.p. of a specimen of semicarbazone of octalin (VI).

Experiment 5. A mixture a 2 g of triketone (V) with 5 ml of absolute methanol and 2 drops of piperidine was left for 2 days at room temperature, the volatile substances were distilled off, and the residue was distilled in vacuum, giving 1.2 g of a substance of b.p. 132-137°/2 mm, n_D^{29} 1.5505, from which 0.2 g of a semicarbazone of m.p. 240-242° was obtained, not depressing the m.p. of the semicarbazone of octalin (VI).

Experiment 6. A mixture of 2 g of triketone (V) with 0.4 g of anhydrous oxalic acid was heated for 15 min. at 130-140°/15 mm., the cooled product was treated with 3 ml of saturated sodium carbonate solution, and extracted with benzene. The solvent is distilled off, and the residue is distilled in vacuum; the fraction boiling at 122-125°/ /2 mm., n_D^{29} 1.5235, partially crystallizes, and recrystallization from light petroleum affords 0.2 g of 1,6-diketo-9-methyl-Δ^5-octalin (VI), m.p. 47-48°, the bis-semicarbazone of which melts at 244-245°, with decomposition [3].

The alkaline solution remaining after extraction of neutral products was made acid to Congo red with concentrated hydrochloric acid, and was extracted with benzene. The benzene solution was dried with magnesium sulfate, and the solvent was distilled off, leaving a crystalline residue from which 0.2 g of unsaturated keto-acid (VIII), m.p. 48-49° (from ether), was obtained.

Experiment 7. 3.7 g of triketone (V) was heated at 100° for 5 min. with 3 g of phosphorus pentoxide, and the cooled product was treated with excess of concentrated aqueous sodium carbonate, the oil forming was extracted with benzene, the benzene solution was dried with sodium sulfate, and the benzene was distilled off in vacuum, leqving 2.3 g of chromanone (XII), b.p. 121-124°/2 mm., n_D^{29} 1.5338.

Found %: C 74.06; 74.05; H 8.19; 8.05. $C_{11}H_{14}O_2$. Calculated %: C 74.2; H 7.95.

The product did not undergo hydrogenation in methanol solution with palladium on charcoal as catalyst. It instantly decolorizes permanganate.

Experiment 8. A solution of 2.9 g of triketone (V) with 3 drops of piperidine in 20 ml of dry benzene was boiled for 7 hours, the solvent and the water formed were distilled off in vacuum, and the residue was fractionated, giving 1.3 g of oil of b.p. 130-135°/3 mm., n_D^{29} 1.5370, from which was obtained 0.3 g of 1,6-diketo-9-methyl-Δ^5-octalin (VI), m.p. 47-48°.

Experiment 9. A mixture of 2.9 g of triketone (V) and 0.5 g of piperidine butyrate was heated on a water bath at 90-95°/15-20 mm., for 4 hours, the product was made acid to Congo red with 1:1 hydrochloric acid, and the solution was extracted with benzene, the benzene extract was dried with magnesium sulfate, the solvent was distilled off, and the residue was distilled in vacuum, giving 2.1 g of oil of b.p. 128-131°/3 mm., n_D^{20} 1.5320, from which 1.5 g of 1,6-diketo-9-methyl-Δ^5-octalin (VI), m.p. 47-48°, was obtained.

Hydrogenation of 1,6-diketo-9-methyl-Δ^5-octalin (VI).

0.1 g of 1,6-diketo-9-methyl-Δ^5-octalin (VI) was hydrogenated in methanol solution, with palladized charcoal (5% Pd) as catalyst. The reaction was completed in 17 min., giving 0.06 g of cis-1,6-diketo-9-methyldecalin (II), m.p. 66-67°, not depressing the m.p. of a known specimen obtained by hydrolysis of 1-keto-6-methoxy-9-methyl-Δ^5-octalin (I) [1].

Hydrolytic decomposition of 1,6-diketo-9-methyl-Δ^5-octalin (VI).

0.4 g of 1,6-diketo-9-methyl-Δ^5-octalin (VI) and 0.3 g of sodium hydroxide in 5 ml of water was boiled under reflux for 1 min., and the cooled solution was extracted with benzene. The aqueous layer was then made acid to Congo red with concentrated hydrochloric acid, and was again extracted with benzene, this extract being dried with sodium sulfate, and the solvent was distilled off. The residual oil was a mixture of carboxylic acids, from which a semicarbazone, m.p. 198-199° (from methanol) was obtained.

Found %: N 16.64; 17.02. $C_{12}H_{19}O_3N_3$. Calculated %: N 16.7.

This semicarbazone slightly depressed the m.p. of the semicarbazone of the unsaturated keto-acid (VIII).

1,6-Diketo-9-methyl-5-carboxymethyl-Δ^5-octalin (XVI).

2.5 g of 2-methyldihydroresorcinol (IV) is dissolved in a solution of 0.1 g of sodium in 8 ml of anhydrous methanol, followed by 2 g of 5-carbomethoxypent-1-en-3-one (XIV), and the mixture is boiled under reflux for 3 hours, the solvent is distilled off, the residue is made neutral with 1:1 hydrochloric acid, and 2 g of saturated aqueous sodium carbonate is added. The oil separating is extracted with benzene, and the extract is dried with magnesium sulfate. The solvent is distilled off, leaving 3.6 g of a viscous oil (n_D^{20} 1.4850), distilling over at 195-202°/0.05 mm., with considerable decomposition. A mixture of 3.6 g of undistilled condensation product (XV) with 0.4 g of anhydrous oxalic acid is heated at 140-150°/15 mm for 30 min., and 10 ml of water are added to the cooled product, giving a crystalline precipitate, recrystallization of which from methanol affords 2.4 g of 1,6-diketo-9-methyl-5-carboxymethyl-Δ^5-octalin (XVI), m.p. 172-173°.

Found %: C 66.29; 66.00; H 7.02; 7.15. $C_{13}H_{15}O_4$. Calculated %: C 66.11; H 6.8.

The product does not give any coloration with $FeCl_3$. It neutralizes 2 molecules of alkali when titrated hot.

Equivalent found by titration 115. $C_{13}H_{16}O_4$. Calculated equivalent 118.

Hydrolytic decomposition of the product of condensation of 2-methyl-dihydroresorcinol (IV) with 5-carbomethoxypent-1-en-3-one (XIV).

0.5 g of the above-described crude condensation product (XV) is boiled for 3 hours under reflux with 10 ml of concentrated hydrochloric acid, which is then removed in vacuum, leaving 0.25 g of the ketodicarboxylic acid (XVIII), m.p. 150-152° (recrystallized from water).

Found %: C 61.30; 61.40; H 7.32; 7.33. $C_{13}H_{18}O_5$. Calculated %: C 61.4; H 7.1

Equivalent found by titration 126. $C_{15}H_{18}O_5$. Calculated equivalent 127.

Hydrolytic decomposition of 1,6-dikto-9-methyl-5-carboxymethyl-Δ^5-octalin (XVI).

0.4 g of 1,6-diketo-9-methyl-5-carboxymethyl-Δ^5-octalin (XVI) is boiled with 15 ml of 1:1 hydrochloric acid under reflux for 2 hours, the hydrochloric acid is removed in vacuum, and the residue is recrystallized from water, giving 0.3 g of the ketodicarboxylic acid (XVIII), m.p. 150-152°, not depressing the m.p. of the sample obtained in the preceding experiment.

Esterification of 1,6-diketo-9-methyl-5-carboxymethyl-Δ^5-octalin (XVI).

A solution of 3.4 g of 1,6-diketo-9-methyl-5-carboxymethyl-Δ^5-octalin (XVI) in 40 ml of absolute methanol is saturated with dry hydrogen chloride, and left for several days at room temperature. The methanol and hydrogen chloride are then distilled off in vacuum, and the residue is treated with 5 g of saturated aqueous sodium carbonate. The oil is extracted with benzene, the benzene solution is dried with magnesium sulfate, and the solvent is distilled off. The residue gives 3.2 g of diester (XIX), b.p. 172-173°/3 mm., n_D^{20} 1.4905.

Found %: C 63.40; 63.44; H 7.94; 7.97. $C_{12}H_{18}O_4$. Calculated %: C 63.8; H 7.9.

Hydrolysis of the dimethyl ester (XIX).

0.3 g of dimethyl ester (XIX) is boiled for 3 hours under reflux with 10 ml of 1:1 hydrochloric acid, which is then distilled off in vacuum, leaving 0.2 g of acid (XVIII), m.p. after recrystallization from water 150-152°, not depressing the m.p. of a known specimen of the unsaturated ketodicarboxylic acid (XVIII).

Ozonation of the dimethyl ester (XIX).

Oxygen containing 6% of ozone is passed for 4 hours through a solution of 1.5 g of dimethyl ester (XIX) in 25 ml of dry chloroform, 20 ml of 5% perhydrol is added, and the mixture is boiled, with vigorous stirring, for 12 hours, after which the chloroform and water are boiled off in vacuum. The residue is boiled for 2 hours with 20 ml of 1:1 hydrochloric acid, which is then distilled off in vacuum, and the residue is fractionated by recrystallization from water and benzene, giving 0.4 g of succinic acid, m.p. 182-183°, not depressing the m.p. of a known sample of succinic acid, and 0.5 g of heptan-3-one-1,6-dicarboxylic acid (XX), m.p. 107-109°.

Found %: C 53.47; 53.42; H 7.34; 7.22. $C_9H_{14}O_5$. Calculated %: C 53.5; H 7.3.

Equivalent found by titration 101.1. $C_9H_{14}O_5$. Calculated equivalent 100.

The semicarbazone melts at 171-172° (recrystallized from methanol).

Found %: N 16.60; 16.43. $C_{10}H_{17}O_5N_3$. Calculated %: N 16.2.

Condensation of tetrinic acid (XXI) with but-1-en-3-one (III)

2.4 g of tetrinic acid [1,3-lactone of butan-2-on-1-ol-3-carboxylic acid] (XXI), followed by 2.5 g of but-1-en-3-one (III) are added to a solution obtained from 0.05 g of sodium and 10 ml of absolute methanol, and the mixture is boiled for 3.5 hours under reflux. The methanol is then distilled off in vacuum, the residue is made neutral (to Congo red) with 1:1 hydrochloric acid, 2 g of sodium carbonate is added, the oil is extracted with benzene, the solution is dried with sodium sulfate, and the solvent is distilled off, leaving 2.2 g of the diketone (XXII), b.p. 130-131°/3 mm., n_D^{20} 1.4710.

Found %: C 58.58; 58.80; H 6.42; 6.65. $C_9O_4H_{12}$. Calculated %: C 58.69; H 6.52.

The substance did not give Tserevitinov's reaction for active hydrogen. It gave a bis-semicarbazone, m.p. 205-206°, with decomposition.

Found %: N 28.20; 23.08. $C_{11}H_{18}O_4N_6$. Calculated %: N 28.2.

Preparation of the unsaturated ketones (XXIII) and (XXV).

The reaction of condensation of tetrinic acid with but-1-en-3-one was conducted as before, except that the amount of sodium was increased to 0.1 g. In this way, 2.4 g of tetrinic acid gave 2.6 g of crude product, from which two fractions were obtained:

Fraction I, 0.2 g, b.p. 80-85°/3 mm
Fraction II, 1.6 g, b.p. 100-115°/3 mm

Recrystallization of Fraction I from methanol gave 0.1 g of crystalline alcohol (XXV), m.p. 65-66°, which instantly decolorized aqueous permanganate.

Found %: C 68.11; 67.94; H 8.74; 8.74. $C_8H_{12}O_2$. Calculated %: C 68.4; H 8.8.

Found %: OH 11.76. $C_8H_{11}O(OH)$. Calculated %: OH 12.15.

Fraction II gave 0.6 g of keto-ester (XXIII), m.p. 90-91° (from methanol). The substance did not neutralize alkalis, and instantly decolorized permanganate solution.

Found %: C 60.30; 60.35; H 7.05; 6.96. $C_{10}H_{14}O_4$. Calculated %: C 60.6; H 7.1.

Found %: OH 8.3; $C_{10}H_{13}O_3(OH)$. Calculated %: OH 8.7.

Hydrolytic decomposition of the lactone (XXII).

A mixture of 1 g of lactone (XXII) and 15 ml of concentrated hydrochloric acid was distilled, under atmospheric pressure; evolution of carbon dioxide was observed, and the distillate crystallized, giving 0.3 g of keto-alcohol, m.p. 65-66° (from aqueous methanol), not depressing the m.p. of a specimen of the above-described keto-alcohol (XXV).

Hydrolytic decomposition of the keto-ester (XXIII).

Under similar conditions to those of the preceding experiment the keto-ester (XXIII) gave 0.3 g of a substance of m.p. 65-66° (from aqueous methanol), not giving any depression with the above keto-alcohol (XXV).

Attempted cyclization of the lactone (XXII).

4 g of lactone (XXII) is heated for 20 minutes with 2 g of oxalic acid at 140-150°, and the product was neutralized with saturated sodium carbonate solution. The oil was extracted with benzene, the extract was dried with magnesium sulfate, and fractionally distilled.

Fraction I, 0.4 g, b.p. 80-90°/3 mm.
Fraction II, 0.5 g, b.p. 100-130°/3 mm, n_D^{20} 1.4910.
Fraction III, 1.7 g, b.p. 130-135°/3 mm, n_D^{20} 1.4928.

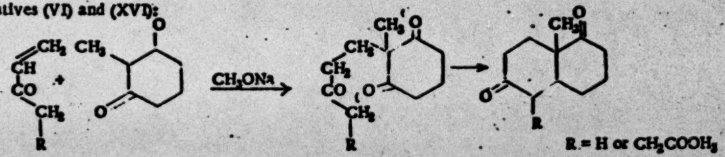
Fraction I gave 0.2 g of the keto-alcohol (XXV), m.p. 65-66°, not depressing the m.p. of the previously obtained specimens. Fraction III appeared to be the impure cyclization product.

Found %: C 61.27; 60.98; H 6.69; 6.76. Calculated for lactone (XXII)%: C 58.7; H 6.52.
Calculated for the product of cyclo-dehydration of lactone (XXII)%: C 65.1; H 6.03.

This substance is readily converted by boiling with hydrochloric acid into the above-described keto-alcohol (XXV).

SUMMARY

1. A study has been made of the condensation of the vinyl ketones (III) and (XIV) with methyldihydroresorcinol, and of the cyclization of the resulting dihydroresorcinol derivatives (V) and (XV) into the diketo-octalin derivatives (VI) and (XVI):



R = H or CH_2COOH_3

2. The triketones (V) and (XV), similarly to the octalins (VI) and (XVI), readily undergo hydrolytic decomposition, with ring opening and formation of the intermediate keto-acids (VII) and (XVII), which then undergo ring closure, giving the cyclohexenone carboxylic acids (VIII) and (XVIII). Condensation of but-1-en-3-one with tetrinic acid (XXI) affords the lactone (XXII), cyclization of which gives the ester (XXIII) and the alcohol (XXV). The lactone (XXII) and the ester (XXIII) are readily converted into the alcohol (XXV) by boiling with hydrochloric acid, by decarboxylation of the hydroxyketo-acid (XXIV).

LITERATURE CITED

[1] I.N. Nazarov, L.D. Bergelson, L.I. Shmonina, and L.N. Terekhova. Bull. U.S.S.R. Acad. Sci., Div. Chem. Sci., 439 (1949); J. Gen. Chem., 20, 648 (1950).* [2] L. Ruzicka, Helv. Chem. acta. 2, 153 (1919). [3] H. Wieland, and K. Miescher, Helv. Chim. acta 33, 2215 (1950). [4] N. Wendler, Slates and M. Tischler, J. Am. Chem. Soc. 73, 3816 (1951). [5] E. Blaise and M. Maire, Bull. (4) 3, 452 (1908). [6] R. Naylor, J. Chem. Soc. 1106 (1947). [7] C. A. Friedmann and R. Robinson, Chem. and Ind. 777 (1951). [8] C. Mannich, Ber. 57, 1114 (1924). [9] A.N. Churbakov and V.N. Ryazantsev. J. Appl. Chem. 13, 1465 (1940). [10] R. B. Thompson, Org. Syntheses 27, 21 (1947). [11] L. Wolff, Ann. 288, 16 (1895). [12] W. Emery, Ber. 24, 282 (1891). [13] R. Fittig, L. Wolff, Ann. 216, 129 (1883).

Received November 25, 1951

Institute of Organic Chemistry, Academy of Sciences USSR.

---

*See Consultants Bureau translation, p. 685.

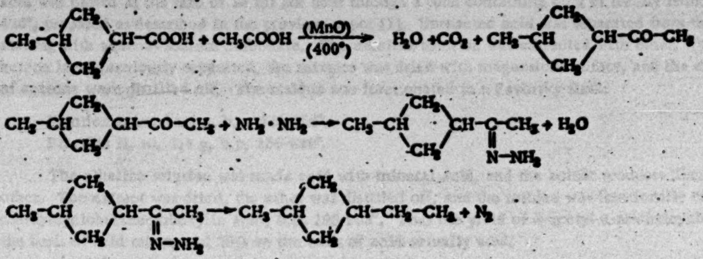
SYNTHESIS OF HYDROCARBONS OF THE CYCLOBUTANE SERIES

PART 2. 1-METHYL-3-ETHYLCYCLOBUTANE AND DI-(3-METHYLCYCLOBUTYL) METHANE

B. A. Kazansky and M. Yu. Lukina

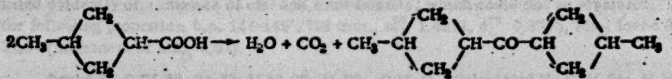
The synthesis of 1-methyl-3-ethylcyclobutane was effected analogously to that of 1,3-dimethylcyclobutane [1]. The starting substance was also 1-methylcyclobutane-3-carboxylic acid, prepared from sodiomalonic ester and 1-chloro-3-bromo-2-methylpropane, through 4-chloro-3-methyl-butane-1,1-dicarboxylic ester and 1-methylcyclobutane-3,3-dicarboxylic acid.

1-Methylcyclobutane-3-carboxylic acid, however, does not give the aldehyde, but affords the ketone 3-acetyl-1-methylcyclobutane, which was reduced by Kizhner's method to the hydrocarbon 1-methyl-3-ethylcyclobutane:



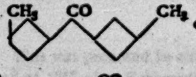
The preparation of 3-acetyl-1-methylcyclobutane, and its conversion into the hydrocarbon, proceeded more smoothly, and with higher yields, than in the case of 1-formyl-3-methylcyclobutane and its conversion into 1,3-dimethylcyclobutane.

A certain amount of a substance of higher boiling point was obtained in the synthesis of both 3-acetyl- and 3-formyl- 1-methylcyclobutane; this product could have been di- (3-methylcyclobutyl) ketone, which could readily be formed by the reactions:



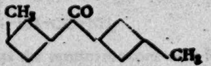
This supposition was checked by converting pure 1-methylcyclobutane-3-carboxylic acid into the ketone, at 420° in the presence of manganous oxide. The ketone so obtained had the same b.p. of 215-220°, identical with that of the ketone obtained as a by-product of the above syntheses, which could, obviously, be a mixture of the three isomers:

(I)



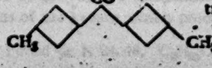
cis-cis-isomer

(II)



cis-trans-isomer

(III)



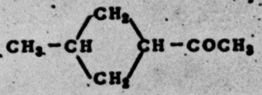
trans-trans-isomer

The separation of the stereoisomers was not attempted, the mixture being converted by Kizhner's method into a mixture of hydrocarbons. The stereoisomeric hydrocarbons were also not separated, in view of their small amount, and of the complexity of the separation process.

The stereoisomeric 1-methyl-3-ethylcyclobutanes obtained by Kizhner's method from 3-acetyl-1-methylcyclobutane were separated by fractional distillation, using an efficient column, into cis- and trans-isomers, obtained, similarly to the 1,3-dimethylcyclobutanes, in a fairly pure state. The determination of their space configuration was performed in accordance with the principles advanced in the preceding paper [1].

EXPERIMENTAL

1. 3-Acetyl-1-methylcyclobutane



A mixture of 23 g (0.2 mol.) of 1-methylcyclobutane-3-carboxylic acid and 51.5 g (0.86 mol.) of glacial acetic acid was passed at the rate of 16 ml per hour through a tube containing 50 g of freshly reduced manganous oxide at 420°, prepared as described in the previous paper [1]. Unreacted acid was separated from the reaction products by shaking with aqueous sodium carbonate. The alkaline solution was extracted with ether, which was added to the ketone layer previously separated, the mixture was dried with magnesium sulfate, and the ether and a small amount of acetone were distilled off. The residue was fractionated in a Favorsky flask:

Fraction I, wt. 14.4 g, b.p. 146-156°.
Fraction II, wt. 1.4 g, b.p. 156-220°.

The alkaline solution was made acid with mineral acid, and the acidic products liberated were extracted with ether. The extract was dried, the ether was distilled off, and the residue was fractionally distilled, giving 4.2 g of methylcyclobutanecarboxylic acid, b.p. 198-203°. Thus the yield of 3-acetyl-1-methylcyclobutane was 63.7%, on the basis of acid taken, and 78% on the basis of acid actually used.

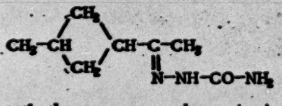
The yields obtained under identical conditions, but at a temperature of 412°, were lower, viz., 69.8, 71, and 70.4% of theoretical on acid actually used in the reaction, or 55-56% on acid taken in the mixture.

Altogether, 98.4 g of 3-acetyl-1-methylcyclobutane was obtained.

The ketone reacted less readily than did the aldehyde with sodium bisulfite, but it gave a voluminous precipitate of bisulfite compound after standing for several hours. The compound, which crystallizes in fine needles, was collected and washed with pentane, and the ketone regenerated from it was distilled from a Favorsky flask; it consisted evidently of a mixture of cis- and trans-isomers, which could not be separated. The redistilled ketone had the following properties: b.p. 144-149°/758 mm., n_D^{20} 1.4281, d_4^{20} 0.8755, MR_D found 32.95, calculated for $C_7H_{12}O$ 32.34 (increment of MR_D 0.61).

Found %: C 74.72; 74.72; H 10.97; 11.05. $C_7H_{12}O$. Calculated %: C 74.94; H 10.79.

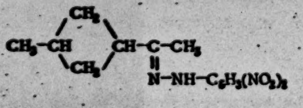
Semicarbazone of 3-acetyl-1-methylcyclobutane



This was prepared in exactly the same way as the semicarbazone of 3-formyl-1-methylcyclobutane [1]. It melted at 125° after 5 recrystallizations from aqueous methanol, and it probably corresponds to that of the stereoisomers of the ketone which predominates in the reaction product.

Found %: N 24.46. $C_8H_{15}ON_3$. Calculated %: N 24.94.

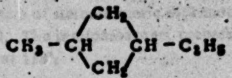
2,4-Dinitrophenylhydrazone of 3-acetyl-1-methylcyclobutane



This was prepared in the same way as the corresponding derivative of 3-formyl-1-methylcyclobutane [1]. It melted at 140° after 4 recrystallizations from ethanol.

Found %: N 18.97; 18.66. $C_{13}H_{16}N_4O_4$. Calculated %: N 19.25.

2. 1-Methyl-3-ethylcyclobutane



A solution of 74 g (1.47 mol.) of hydrazine hydrate in 70 ml of ethanol was added to 81.8 g (0.73 mol) of 3-acetyl-1-methylcyclobutane dissolved in 80 ml of ethanol, and the mixture was boiled for 4 hours under reflux. The aqueous layer formed was removed, and the hydrazone was dried with anhydrous potassium hydroxide, at room temperature initially, and later on a boiling water bath. The hydrazone was separated from the potassium hydroxide solution, and was decomposed, without any preliminary distillation, in exactly the same way as the hydrazone of 3-formyl-1-methylcyclobutane [1], giving 53.8 g of 1-methyl-3-ethylcyclobutane, a yield of 75.4% calculated on the amount of 3-acetyl-1-methylcyclobutane taken. The product was dried over fused calcium chloride, and was distilled from metallic sodium, giving a product of the following properties: b.p. 87.9-91.6°/755 mm., n_D^{20} 1.4019, d_4^{20} 0.7262, MR_D found 32.88, calculated for C_7H_{14} 32.32 (increment of MR_D 0.56).

The hydrocarbon so obtained was a mixture of the trans- and the cis-isomer, and, as in the case of 1,3-dimethylcyclobutane, separation into the individual stereoisomers was effected by fractional distillation of 50.25 g (70.4 ml) of the hydrocarbon, using a column of 50 theoretical plates, with an output of 1 ml per hour, adding 15 ml of octane (n_D^{20} 1.3970) to the distilling flask after 60 ml of distillate had been received.

Two fractions, boiling at about 88° and 91° at 760 mm, were obtained, as well as an intermediate fraction, which was returned for further fractionation. The fractions shown in Table 1 were finally collected.

TABLE 1

No. of fraction	B.p., °C	Pressure, mm	Amount	
			g	ml
1	76.3 - 87.5	760	2.2	3.2
2	87.5 - 87.9	760	4.25	6.3
3	87.9 - 88.1	760	17.4	24.3
4	88.1 - 91.0	760	13.5	18.5
5	91.0 - 91.1	760	7.8	10.8
6	91.1 - 92.0	760	2.0	3.0

It may be concluded from the results shown in Table 1 that we had separated two individual hydrocarbons, boiling at 87.9-88.1° and at 91.0-91.1°/760 mm, and an intermediate fraction, being a mixture of these fractions, distilling over at 88.1-91.0°. The fraction of b.p. 87.9-88.1° may be assumed, on the grounds given in our previous paper [1], to be the trans-isomer, and the fraction of b.p. 91.0-91.1° would be the cis-isomer of 1-methyl-3-ethylcyclobutane.

Trans-1-Methyl-3-ethylcyclobutane: b.p. 87.9-88.1°/760 mm, n_D^{20} 1.4005, d_4^{20} 0.7224, MR_D found 32.96, calculated for C_7H_{14} 32.32 (MR_D increment 0.64).

Found %: C 85.61; 85.64; H 14.39; 14.40. C_7H_{14}. Calculated %: C 85.62. H 14.38.

Cis-1-Methyl-3-ethylcyclobutane: b.p. 91.0-91.1°/760 mm, n_D^{20} 1.4043, d_4^{20} 0.7316, MR_D found 32.81, calculated for C_7H_{14} 32.32 (MR_D increment 0.49).

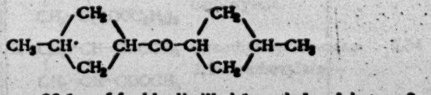
Found %: C 85.56; 85.53; H 14.27; 14.43. C_7H_{14}. Calculated %: C 85.62; H 14.38.

The aniline points of the stereoisomers of 1-methyl-3-ethylcyclobutane and 1,3-dimethylcyclobutane are given in Table 2.

TABLE 2

Hydrocarbon	Aniline point	
	trans-	cis-
1,3-dimethylcyclobutane	53.6	48.9
1-methyl-3-ethylcyclobutane	57.2	52.2

3. Di-(3-methylcyclobutyl) ketone



28.1 g of freshly distilled 1-methylcyclobutane-3-carboxylic acid was passed at a rate of 11.5 ml per hour at 420° through a tube containing 50 g of freshly reduced manganous oxide. After extraction with sodium carbonate solution, in order to remove unreacted acid, the neutral reaction product was distilled from a Favorsky flask, and the main fraction, boiling at 213-223°/759.5 mm, n_D^{20} 1.4586, d_4^{20} 0.9142, was collected; yield 43.5%, calculated on the amount of acid taken for the reaction. The MR_D

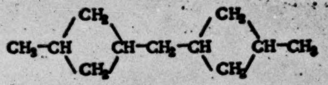
found was 49.65, calculated for $C_{11}H_{18}O$ 48.61 (MR_D increment 1.04, or 0.52 per cyclobutane ring).

We assumed that this fraction is a mixture of stereoisomeric di(3-methylcyclobutyl) ketones, although its carbon content is somewhat lower than expected. The semicarbazone, prepared in the usual way, and four times recrystallized from aqueous methanol, melted at 118°.

Found %: N 18.85; 18.74. $C_{12}H_{21}ON_3$. Calculated %: N 18.91.

The ketone did not give a crystalline product with 2,4-dinitrophenylhydrazine; the heavy orange-colored oil obtained was not analyzed.

4. Di-(3-methylcyclobutyl)-methane.



This was prepared from the above ketone, as well as from the fraction of b.p. 213-220° which is always obtained as a by-product during fractionation of the products of synthesis of 3-formyl-1-methylcyclobutane and of 3-acetyl-1-methylcyclobutane.

A solution of 33 g (0.2 mol.) of di-(3-methylcyclobutyl) ketone or of the fraction of b.p. 213-220° in 35 ml of absolute ethanol was added gradually to 22 g (0.44 mol.) of hydrazine hydrate in 25 ml of ethanol, and the mixture was heated on a water bath for four hours. The ethanol was distilled off on the following day, from an oil bath at 140°, and the residual oil was dehydrated by adding anhydrous caustic alkali. The hydrazone was decomposed as before [1], without previous distillation. The hydrocarbon so obtained was washed successively with 50% acetic acid, 50% sulfuric acid, and 10% sodium hydroxide solution, dried with calcium chloride, and distilled from metallic sodium, giving 9.2 g of a hydrocarbon of b.p. 178-184°/ 747 mm; the b.p. of this product was not changed by redistillation. Owing to the small amount of this product, it was not subjected to further fractional distillation, although it must have consisted of a mixture of stereoisomers, as was mentioned earlier in this paper. The hydrocarbon had the following properties; n_D^{20} 1.4402, d_4^{20} 0.8027, MR_D found 49.98, calculated for $C_{11}H_{20}$ 48.56. (MR_D increment 1.42, or 0.71 per cyclobutane ring).

Found %: C 86.70, 86.44; H 13.24; 13.22. $C_{11}H_{20}$. Calculated %: C 86.75; H 13.25.

Molecular refraction of compounds possessing the cyclobutane ring.

All the cyclobutane derivatives so far prepared have a higher molecular refraction than the theoretical. Wallach [2] in 1889 found that for the sodium line D the molecular refraction of pinene and of some of its derivatives exceeded their atomic refraction by an amount of about 0.4. Oestling [3] in 1912 tabulated the molecular refractions of the 16 cyclobutane derivatives then known.

TABLE 3

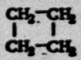
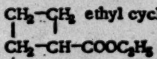
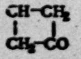
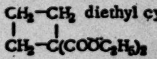
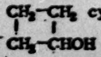
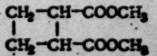
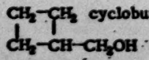
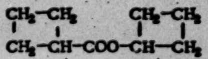
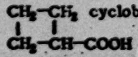
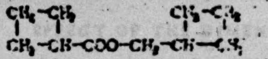
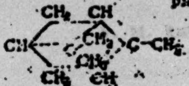
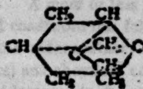
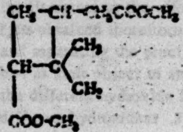
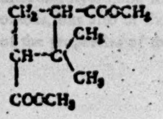
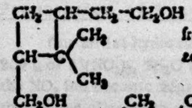
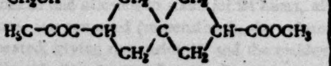
Substance	Increment MR_D	Substance	Increment MR_D
1.  cyclobutane	0.21	6.  ethyl cyclobutanecarboxylate	0.43
2.  cyclobutanone	0.49	7.  diethyl cyclobutane-1,1-dicarboxylate	0.37
3.  cyclobutanol	0.42	8.  dimethyl cyclobutane-1,2-dicarboxylate	0.54
4.  cyclobutylcarbinol	0.53	9.  cyclobutyl cyclobutanecarboxylate	$\frac{0.84}{2} = 0.42$
5.  cyclobutanecarboxylic acid	0.49		

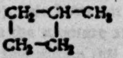
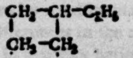
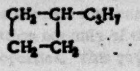
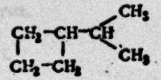
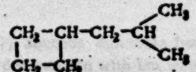
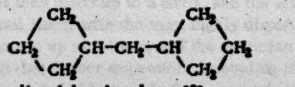
TABLE 3 – (continued)

Substance	Increment MR_D
10.  cyclobutylmethyl cyclobutanecarboxylate	$\frac{0.96}{2} = 0.48$
11.  pinene	0.49
12.  nopinone	0.57
13.  methyl pinate	0.44
14.  methyl norpinate	0.48
15.  glycol prepared from ester of pinic acid	0.31
16.  methyl spiroheptanedicarboxylate	$\frac{1.14}{2} = 0.57$

Oestling, on the basis of the data of Table 3 (with the exception of compounds Nos. 1, 7, 15 and 16), derived a value of 0.48 for the increment in molecular refraction. This value was quoted by Eisenlohr in his "Spektrochemie organischer Verbindungen" [4], and has continued to be cited in works of reference.

A consideration of the molecular refractions of cyclobutane hydrocarbons synthesized since 1912 shows that the average value of the increment is very close to Oestling's value.

TABLE 4

Substance	Increment MR_D
1.  methylcyclobutane [5]	0.53
2.  ethylcyclobutane [6]	0.45
3.  propylcyclobutane [7]	0.51
4.  isopropylcyclobutane [8]	0.41
5.  isobutylcyclobutane [9]	0.45
6.  dicyclobutylmethane [9]	0.47
Average increment of MR_D	0.47

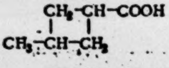
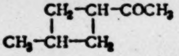
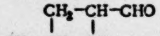
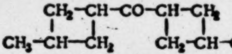
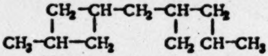
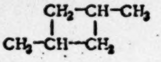
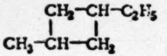
The compounds described in this and in the preceding paper, however, show a higher increment of MR_D, as is evident from Table 5.

The increase in the increment of molecular refraction may be ascribed to the circumstance that the cyclobutane derivatives in question are disubstituted ones, and hence represent mixtures of cis- and trans- isomers. This is shown by their indefinite boiling points, and by the fact that the last two compounds of Table 5, 1,3-dimethylcyclobutane and 1-methyl-3-ethylcyclobutane, have been separated by fractional distillation into their steroisomers. It appeared that whereas the cis-isomers of these hydrocarbons have an increment of molecular refraction fairly close to the mean value calculated for the various monosubstituted cyclobutanes, the trans-isomers have a much higher increment, amounting for trans-1,3-dimethylcyclobutane to +0.68, and for 1-methyl-3-ethylcyclobutane to +0.64. This explains the elevated values of MR_D found for the disubstituted cyclobutanes. It is, in connection with this, necessary in speaking of the increment of molecular refraction of cyclobutane derivatives to take into account their structure, and in particular the number of substituents in the ring, on which depends the possibility of the existence of stereoisomeric forms.

SUMMARY

1. The new compound 1-methyl-3-ethylcyclobutane has been synthesized and separated into its cis- and trans- isomers.

TABLE 5

	Substance	Increment MR_D
1.		0.58
2.	 3-acetyl-1-methyl-cyclobutane	0.61
3.	 3-formyl-1-methyl-cyclobutane	0.64
4.	 di-(3-methylcyclobutyl) ketone	$\frac{1.04}{2} = 0.52$
5.	 di-(3-methylcyclobutyl)-methane	$\frac{1.40}{2} = 0.70$
6.	 1,3-dimethylcyclobutane	0.59
7.	 1-methyl-3-ethyl-cyclobutane	0.56
	Average increment of MR_D	0.60

2. The new compound di-(3-methylcyclobutyl)-methane has been synthesized as a mixture of stereoisomers.

3. A number of new disubstituted cyclobutane derivatives have been prepared and described.

4. The disubstituted cyclobutanes are shown to have an elevated increment of molecular refraction, due to the effect of the trans-isomers.

LITERATURE CITED

[1] B.A. Kazansky and M. Yu. Lukina. Bull. U.S.S.R. Acad. Sci., Div. Chem. Sci. 1, 47-56 (1951).

[2] O. Wallach, [illegible] Ann. 252, 140 (1889).

[3] G. J.Oestling, J. Chem. Soc. 101, 457 (1912).

[4] F. Eisenlohr, Spektrochemie organischer Verbindungen, Stuttgart, 1912.

[5] O.G. Filippov. J. Russ. Chem. Soc., 46, 1441 (1914).

[6] N.M. Kizhner. J. Russ. Chem. Soc., 45, 973 (1913).

[7] N.D. Zelinsky and B.A. Kazansky. J. Russ. Chem. Soc., 59, 659 (1927).

[8] B.A. Kazansky. J. Gen. Chem. 6, 1598 (1938).

[9] B.A. Kazansky and V.P. Golmov. Proc. Acad. Sci. U.S.S.R., 34, 196-198 (1942).

Received December 29, 1951

Institute of Organic Chemistry, Academy of Sciences U.S.S.R.

EFFECT OF THE DIMENSIONS OF THE ELEMENTARY CRYSTALLITES ON THE POROSITY AND ACTIVITY OF Al_2O_3 CATALYSTS OF DEHYDRATION REACTIONS

A. M. Rubinshtein, V. E. Vasserberg, and N. A. Pribytkova

A more or less poly-disperse precipitate is obtained in any process of precipitation of hydroxides. Under standard conditions this follows during the whole duration of the process from the probable distribution of the particles, while under ordinary conditions of precipitation additional factors are the variability of physical (stirring, and the like) and chemical conditions (progressive diminution of the concentration of the cations undergoing precipitation, and increase in the concentration of other cations in the solution). We have not been able to trace any reference in the literature to the effect of the poly-dispersity of hydroxides on the structure and the properties of the oxide catalysts obtained therefrom by dehydration. We have attempted to investigate this question, taking alumina as the oxide, and separating the precipitated aluminum hydroxide into fractions by a sedimentation method. Our investigations had as their object to answer the questions: 1) Are there any differences in the activity of the Al_2O_3 obtained from the different hydroxide fractions? 2) Are there any differences in structure between the oxides produced from the different hydroxides? 3) What differences are there between the specific surfaces of the oxides prepared from different hydroxide fractions? Our studies involved the investigation not only of the catalytic properties of the oxides, but also of their X-ray structure and of their adsorbent properties. This gave us a sufficiently full picture of the properties of the specimens of Al_2O_3 as dehydration catalysts.

EXPERIMENTAL

Preparation of Specimens of Catalysts.

Our initial hydroxide was obtained by precipitation with 5% aqueous ammonia from a boiling solution of 250 g of $Al(NO_3)_3 \cdot 9H_2O$ in 3 liters of water, and was washed by decantation with hot water until the reaction for the NO_3 ion became negative. The volume of the suspension was then made up to 3 liters, and the suspension was shaken and allowed to stand for 24 hours, after which the upper two liters, with the most highly disperse precipitate, was removed (suspension I), the volume of the residue was made up to 3 liters, and the operation was repeated, giving suspension II, and the residue was again diluted, giving further suspensions, according to the scheme given in Fig. 1. Catalyst No. 1 was prepared from the smallest particles of hydroxide from suspensions I and II, catalyst No. 2 from suspension III and IV, and catalyst No. 3 from the largest particles deposited at all stages of the process.

We originally intended to prepare the specimens separately from each suspension, but we found that we had to unite pairs of suspensions, in order to have enough material for all the determinations necessary. Attempts at determining the particle size of the various hydroxide suspensions by means of Rehbinder's sedimentometer were unsuccessful, owing to the very small rate of sedimentation of the smaller particles, and to the stopping up of the lower part of the sedimentometer tube by the gelatinous precipitate, which prevented any change in the level in the graduated part of the instrument.

All the specimens were pressed into cylinders of the same size, using a press with the same aperture, the cylinders were dried in air, and were heated at 360° under standarized conditions, to constant weight. Catalysts Nos. 1, 2, and 3 were thus prepared, in amounts of 9.2, 4.9, and 13.4 g, corresponding with 33.4, 17.8, and 48.8% of the total amount of Al_2O_3 produced. The specific weights of the heaped catalysts 1, 2 and 3 vary to some extent (see Table 6). Their residual water content was determined by heating to constant weight at 900-1000°; the results are given in Table 6.

Experimental Data

The activites of the Al_2O_3 catalysts were determined basically from their effect in the dehydration of 77.5%

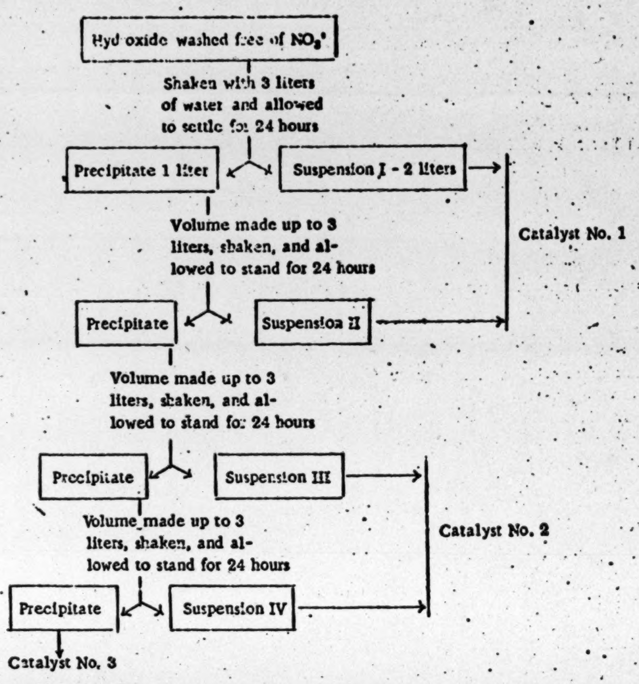

Hydroxide washed free of NO_3'
Shaken with 3 liters of water and allowed to settle for 24 hours
Precipitate 1 liter
Suspension I - 2 liters
Volume made up to 3 liters, shaken, and allowed to stand for 24 hours
Precipitate
Suspension II
Catalyst No. 1
Volume made up to 3 liters, shaken, and allowed to stand for 24 hours
Precipitate
Suspension III
Volume made up to 3 liters, shaken, and allowed to stand for 24 hours
Catalyst No. 2
Precipitate
Suspension IV
Catalyst No. 3

Fig. 1. Schema of preparation of catalysts

formic acid and of 96% ethanol; additional experiments were later also performed with n-butanol and n-pentanol. The experiments were performed on flowing systems, in a Vaskevich reactor [1], which is adapted to use with small amounts of catalyst. The reactor was warmed in an oven, the temperature of which was regulated by means of a contact galvanometer, the temperature of the catalyst being measured by means of a thermocouple. For all experiments 1 g (2 ml) of catalyst was taken. The rate of flow of the substrates was maintained constant at the rate of 2 liters per liter of catalyst per hour.

The results (reduced to N.T.P.) obtained in the basic experiments are given in Tables 1 and 2. They show that the relative activities of the catalysts 1, 2, and 3 as found for dehydration of HCOOH are also applicable to dehydration of ethanol. Since the amount of catalyst taken was in all cases 1 g., the data given characterize the specific activity of each of the specimens of Al_2O_3 studied. Tables 1 and 2 also give the amounts of by-products formed, viz., CO_2 and H_2 from dehydrogenation of HCOOH, and CH_4, CO_2, and H_2 from ethanol.

These results show that under the given conditions the main reaction of dehydration was complicated very little by side-reactions. We should add that the figures given in Tables 1 and 2 for amounts of by-products must be regarded as only approximate, in view of the very small volumes of gases remaining after absorption of CO_2 and CO, in the case of HCOOH, and of CO_2 and C_2H_4 in the case of ethanol. This made it necessary to dilute the residues with large amounts of nitrogen, in order to have a sufficient volume of gas for the manipulations associated with their determination.

If we take the specific activity of Catalyst No. 3 as unity, then the specific activities of catalysts Nos. 1 and 2 would be expressed by the figures 0.68 and 0.64, for HCOOH, and 0.59 and 0.49 for ethanol.

TABLE 1

Experimental Results for Decomposition of HCOOH

No. of catalyst	Ml of gaseous products (at N.T.P.) evolved per ml of HCOOH											
	At 275°				At 300°				At 325°			
	Σ	CO_2	CO	H_2	Σ	CO_2	CO	H_2	Σ	CO_2	CO	H_2
1	150.2	8.4	132.6	8.4	244	10.0	227.0	7.6	376.0	25.2	325.0	24.1
2	123.9	3.27	113.0	7.4	227.0	8.4	207.0	11.4	338.0	14.1	306.0	18.3
3	267.0	10.0	248.0	10.0	357.0	6.1	342.0	7.9	504.0	10.0	482.0	10.0

TABLE 2

Decomposition of Ethanol at 325°

No. of catalyst	Ml of product (at N.T.P.) evolved per ml of ethanol				
	Σ	C_2H_4	H_2	CO_2	CH_4
1	96.8	83.2	2.6	5.4	4.35
2	79.3	69.2	5.0	2.7	1.8
3	158.9	152.0	–	2.4	4.0

X-Ray Study of Specimens of Catalysts

The Debyeograms of the catalyst were taken with iron radiation ($K_\alpha = 1.932$ A) on Kodak films, with an exposure time of 6 hours, at 30 kV and 10 mA. All specimens gave crystallite X-ray diagrams, but the Roentgenogram of Catalyst No. 1 exhibited a pronounced background effect, which rendered impossible its photometric study for the determination of the dimensions of the elementary crystallites. The diagrams showed that all the catalysts consisted of γ-Al_2O_3, and that other modifications of Al_2O_3 were absent, as were also its crystalline hydrates. The relevant data are given in Table 3, from which it appears that the magnitude of the parameter for the face-centered cubic crystal lattice of γ-Al_2O_3 differs little from specimen to specimen.

The microphotometric curves taken from the Roentgenograms were recorded with the aid of a registering Siegbahn microphotometer, with a magnification of 2.5. Measurements of the half-width of the lines of Brill's curves [2] served as a basis for arriving at the values of $\eta\frac{R}{r}$, and the values of η and of λ (linear dimensions of the elementary crystallites) were then derived. The results given in Table 4 show that there is satisfactory agreement between the values of λ obtained for different angles of reflection, which testifies to the cubic form of the Al_2O_3 crystallites in the specimens examined.

TABLE 3

Roentgenostructural Data for the Catalysts
(Derived from Experimental Results)

hkl	No. 1		No. 2		No. 3	
	J	2 sinθ	J	2 sinθ	J	2 sinθ
222	medium	0.830	–		medium	0.838
004	medium	0.970	medium	0.992	strong	1.018
024	medium	1.080	–		weak	1.080
333/511	weak	1.296	medium	1.278	medium	1.294
004	strong	1.406	strong	1.390	weak	1.410
244/600	weak	1.490	–	–	weak	1.500
444	medium	1.730	–	–	medium/weak	1.726
$\underline{a}$ mean		7.83 A		7.82 A		7.80 A

Determination of the Specific Surface of the Catalysts

The determination of the specific surface of the catalysts was based on measurements of the adsorption isotherms for the vapors of methanol and of n-pentane at 25°, made using the ordinary apparatus, with a quartz micro-balance. The methanol and the pentane used were first subjected to thorough rectification in a laboratory column, effectiveness 30-40 theoretical plates. The

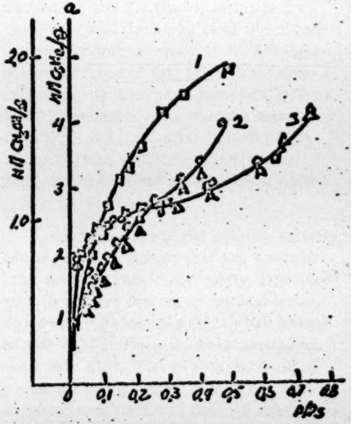


Fig. 2. Adsorption isotherm for methanol or n-pentane vapors, at 25°; 1) Catalyst No. 3, C_5H_{12}; 2) catalysts Nos. 1 and 2, C_5H_{12}; 3) catalysts Nos. 1, 2, and 3, CH_3OH.

TABLE 4

Determination of Dispersity (Size of Elementary Crystals)

No. of catalyst	hkl	Half-width of line, in min	θ according to Roentgenogram	$\eta\frac{R}{r}$	η	λ, A	λ_{mean}, A
2	004	1.44	20.7	0.285	0.00437	35.5	
	044	1.52	44.1	0.237	0.00440	35.1	35.3
3	004	0.96	30.6	0.164	0.00278	55.3	
	333	1.08	40.55	0.180	0.00305	50.5	51.4
	044	1.12	44.8	0.188	0.00318	48.3	

TABLE 5

Adsorption of Methanol and n-Pentane, in m-mole/g of Catalyst

Methanol				Pentane			
p/p_s	Catalyst No. 1	Catalyst No. 2	Catalyst No. 3	p/p_s	Catalyst No. 1	Catalyst No. 2	Catalyst No. 3
0.02	2.054	1.922	1.944	0.009	0.335	0.243	0.415
0.06	2.209	2.198	2.214	0.023	0.413	0.310	0.551
0.08	2.416	2.332	2.322	0.029	0.424	0.363	0.727
0.11	2.460	2.452	2.430	0.040	0.480	0.387	0.703
0.15	2.563	2.533	2.675	0.051	0.525	0.446	
0.20	2.511	2.545	2.700	0.064	0.614	0.497	0.791
0.27	2.598	2.640	2.820	0.084	0.673	0.582	1.014
0.31	2.736	2.760	2.682	0.104	0.766	0.660	1.103
0.42	3.000	2.891	3.060	0.128	0.870	0.766	1.280
0.43	3.124	3.000	3.116	0.172	0.960	0.854	1.350
0.57	3.331	3.316	3.186	0.210	1.038	0.943	1.446
0.63	3.581	3.693	–	0.264	1.116	1.092	1.694
0.72	4.194	4.216	–	0.328	1.265	1.207	1.774
				0.390	1.373	1.295	1.894
				0.464	1.596	1.557	1.926

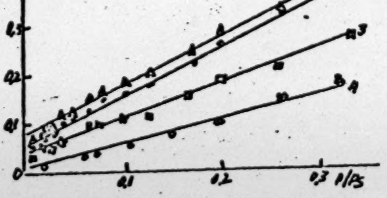


Fig. 3. BET curves for Catalysts 1, 2, and 3, with methanol and with n-pentane: 1) Catalyst No. 2, C_5H_{12}; 2) Catalyst No. 1, C_5H_{12}; 3) Catalyst No. 3, C_5H_{12}; 4) Catalysts No. 1, 2, and 3, CH_3OH.

magnitude of the specific surface was calculated by the method of Brunnauer, Emmet, and Teller. The values obtained for adsorption, in m-mole/g, and the rectilinear curves derived therefrom by the equation of Brunnauer, Emmet, and Teller are shown in Figures 2 and 3 (see Table 5).

Relation Between Structure, Surface, and Activity of the Catalysts

The results reported in this paper show that the catalysts prepared from different hydroxide fractions are not identical. This is evident from a comparison of their physical properties and of other data presented in Table 6, and also from their specific activity ratios for the reactions of dehydration of HCOOH and ethanol. Thus Catalyst No. 3 is 1.5-2 times more active than Catalyst No. 1 in the reactions of dehydration of HCOOH or ethanol, at different temperatures, and Catalysts No. 1 and 2 in turn differ considerably in activity, although their specific weights differ very little, and although their specific surfaces are very similar, for both adsorbates (we were not able to establish whether the dimensions of the elementary crystallites of Catalysts 1 and 2 differed, owing to the interference of the background which prevented photometric study of the Roentgenograms of Catalyst No. 1; a visual comparison of the Roentgenograms of Catalysts 1 and 2 seemed to show that the breadth of the lines was very similar in both cases). We emphasize that the preparations of Al_2O_3 studied all had practically identical crystal lattice constants.

A comparison of the specific activity of the catalysts showed that No. 2 was the least active. This is apparently connected with its greater content of residual water, as shown by its loss of weight when heated to 900-1000°. Since the Roentgenograms show only Al_2O_3 lines (Table 3), those of γ-AlOOH being absent, it may be concluded either that the latter phase is amorphous to X-rays, in view of its low content, or, more probably, that the residual water of catalysts dried at 360° is present as an adsorbate on γ-Al_2O_3. The reciprocal relationship between the residual water content of the catalysts and their activity in both the reactions is found to be practically linear, as is shown by Figure 4.

TABLE 6

Physical constants and activity ratios of the catalysts

Catalyst No.	Amt. obtained, g	% of total amount	Heaped sp. wt.	% Weight loss when calcined	Sp. surface in sq. m. per g		Linear dimensions of crystallites, in A	Relative activity in dehydration of	
					CH_3OH	$p\text{-}C_5H_{12}$		HCOOH	C_2H_5OH
1	9.2	33.4	0.575	9.9	286	182	≤ 35	0.68	0.59
2	4.9	17.8	0.566	13.04	286	179	35	0.64	0.49
3	13.4	48.8	0.542	5.42	286	264	51.4	1.00	1.00

The fall in activity as the water content rises may be due to its adsorption at the active centers of the catalysts, i.e., to blocking of these centers by water molecules, or to interference with surface diffusion of the reacting substances and of reaction products by water molecules present in the micro-pores of the catalysts.

The Roentgenographic data, which give no evidence for the presence of γ-AlOOH, lead to the explanations of the inhibiting effect of water given above, since at the temperature of the dehydration experiments γ-AlOOH gradually loses water, which may then lower the activity of the catalysts, either by blocking active centers, or by hindering diffusion.

In addition to comparing the linear dimensions of the elementary crystallites of the catalysts, and the magnitudes of their specific surfaces, we attempted to determine or compare their porosity, by the methods described by Dubinin [3] and Kiselev [4] for estimation of the pore size of adsorbents. With this object in view we measured the surfaces by the method of adsorption of the vapors of methanol and n-pentane. We selected the most trustworthy of the published values for the area occupied by a molecule of these substances, viz., 33.2 A for pentane [5], and 145 sq. m. per mM for methanol [6]. We found that the adsorption isotherms for methanol, and the values for the specific surfaces of the three catalysts hence calculated, are practically identical (Figs. 2 and 3, Table 6). The adsorption isotherms for n-pentane, and the derived specific surfaces, are, however, practically identical for catalysts 1 and 2, but are both much greater for catalyst No. 3.

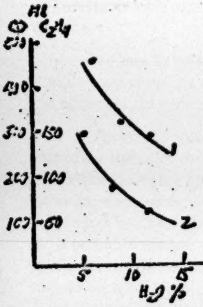


Fig. 4. 1) HCOOH; 2) C_2H_5OH

The smaller figures for adsorption of n-pentane than of methanol for catalysts 1 and 2 can be explained only on the assumption that parts of the surface of these catalysts are inaccessible to the relatively larger n-pentane molecules; such parts of the surface may be supposed to be the walls of the finest micro-pores. This explanation is in good correspondence with the conditions of preparation of the catalysts, and with the results of X-ray studies.

The differences between the values for the specific surface with regard to methanol (286 sq.m. per g for all three catalysts) and to pentane (179 and 264 sq.m. per g) can also be ascribed to differences in the size of the adsorbed molecules. Our results are in agreement with published references to differences in the values of specific surface derived from measurements of adsorption of substances whose molecules are of widely different size; thus the specific surface of a specimen of Al_2O_3 was found to be 141 or 70 sq.m. per g., according to whether the adsorbate was N_2 or $C_{17}H_{35}COOH$ [7]. Our findings show that considerable differences in specific surface, markedly affecting the activity of the catalysts, are obtained with much smaller differences between the size of the molecules, as with CH_3OH and C_5H_{12}. These findings show clearly that the method for determination of the specific surface of catalysts based on measurements of low temperature adsorption of nitrogen (area occupied by a molecule is 16.2 A^2) is inacceptable, in particular for the case of organic catalysis, in which the reacting molecules are of relatively large dimensions. It is in such cases preferable to derive the measurements of specific surface from values obtained for adsorption of substances of molecule size comparable to that of the substance entering into catalyzed reaction. Similar conclusions regarding the unsuitability of relatively large molecules for measuring the actual surface of micro-pored adsorbents have been made by Kiselev et al. in a recently published paper [8].

It follows from the observation that the specific surface of the catalysts, as derived from measurements of adsorption of methanol, is the same in all cases, although their activities are different, that some complex relationship must exist between the activity of a catalyst and its specific surface. The usual assumption that differences between activity of catalysts are due to differences in the number of active centers per unit of surface, as measured by physical adsorption methods, is obviously inadequate; it is necessary also to include a consideration of porosity characteristics of the catalysts. Thus in our case the smaller surface of the more highly dispersed catalysts Nos. 1 and 2, as derived from the measurements of adsorption of n-pentane, shows that the diameter of the micro-pores of these catalysts is smaller than of catalyst No. 3, and this leads to diminution in their activity, although they have the same specific surface as catalyst 3 with regard to methanol.

The large specific surface of catalyst 3, with regard to pentane, is not fortuitous. It is obviously connected with the large linear dimensions of the Al_2O_3 crystallites of this catalyst, which when packed together to give secondary particles give rise to pores of larger diameter than do the smaller crystallites of catalysts 1 and 2. This is connected with the fact that catalyst No. 3 is prepared from the most coarse-grained and rapidly settling fraction of aluminum hydroxide. On the other hand it is well known that with considerable increase in particle size an abrupt fall in specific surface and in catalytic activity ensues. There should, therefore, exist certain limiting sizes of the elementary crystallites for which catalytic activity is at a maximum. An optimum dispersity was found to exist for a number of catalysts [8], and for various reactions [9]. As appears from the present paper, one of the most important factors, of a purely structural nature, responsible for the existence of an optimum value for dispersity, is the most favorable diameter of the micro-pores for a given reaction; these micro-pores are in turn formed by crystallites of certain optimum dimensions which are aggregated to give the secondary particles (catalyst granules).

When the dimensions of the elementary crystallites are very small, the micro-pores, which are the crevices between crystallites which have adhered to each other at certain angles, may be too small to permit of the entry of the reacting molecules. This explains why the maximum activity does not coincide with the greatest dispersity, as measured Roentgenographically. The optimum dispersity is that at which the dimensions of the elementary crystallites are such as to lead to the formation of micro-pores of a diameter similar to or greater than that of the reacting molecules. It is obvious that with further increase in the dimensions of the elementary crystallites, and hence in the diameter of the pores, the latter may assume the nature of transport pores, in view of their large size; an inevitable consequence of this process would be a considerable fall in the specific surface, and in the catalytic activity.

We thus have an explanation of the fall in catalytic activity as the dimensions of the elementary crystallites deviate from the optimum. It is evident that the change in activity observed as the dispersity differs from the optimum, in either direction, should proceed smoothly, as has been found experimentally [8].

The dependence of the micro-pore diameters on the dimensions of the elementary crystallites of which the secondary particles are built up may readily be represented schematically, taking the shape of the elementary crystallites as being approximately spherical. This has been done in Fig.5, which shows that the diameter of the pores increases with the diameter of the spheres. The actual crystallites are not, of course, spherical – they are polyhedral bodies. This does not, however, affect the general nature of the process; for an identical statistically most probable mutual orientation of crystallites of a given shape packed in a secondary particle the dimensions of the pores will be found to be greater for crystallites of greater linear dimensions. Bearing in mind that the magnitude of the specific surface is basically determined by the dimensions of the micro-pores, the role of the dimensions of the elementary (primary) particles becomes obvious, as a factor determining the magnitude of the surface.

A similar explanation of the existence of an optimum of dispersity, based on purely structural considerations, is supported by the results found [10] for the dehydrogenation of HCOOH, iso-$C_5H_{11}OH$, and C_6H_{12} at nickel catalysts. Over a relatively narrow interval of optimum dispersity (20-25 Å) of nickel, the activity of the catalyst in these three reactions is not identical, especially if we take into account differences in the temperatures of the reactions. It appears that the activity at optimum dispersity of the catalyst also depends, for a given type of reaction (in this case, of dehydrogenation), on the size of the reacting molecules.

We are not inclined to consider that the structural factor described by us (dependence of size of micropores on the dimensions of the elementary crystallites of which the secondary particles are made up) is the sole factor determining the dispersity optimum, but we believe that it plays at least as important a role as does chemical supersaturation [11] or capture of micro-constituents, which passes through a maximum for a given size of crystallites.

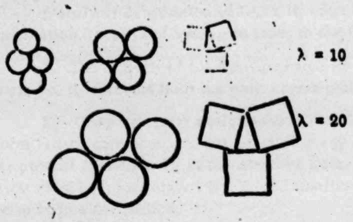


Fig. 5

This second explanation is confirmed by the very interesting results obtained by Fricke and Diefel [12] for adsorption by alumina of KH_2PO_4 from its aqueous solutions. These authors found that the ratio of adsorbed K^+ to $HPO_4^=$ varies according to the size of the Al_2O_3 particles; the ratio K/HPO_4 increases with increase in particle size. It seems to us that this effect may be connected with differences in the size of the pores of the specimens of Al_2O_3 prepared by these authors by dehydration of γ-AlOOH at different temperatures (300°, 500°, 600°, and 800°) and differences between the size of K and HPO_4 ions in the solution.

Additional experiments were performed on the dehydration of n-butanol and n-pentanol at catalysts No. 1 and 3 (Table 7), in order to verify the suppositions made by us that there is a correlation between the size of the micro-pores and the dimensions of the elementary crystallites, on the one hand, and the activity of the catalyst, on the other. The results given in Table 7 (ml of reaction products per ml of alcohol under the same conditions as for the dehydration of ethanol) are those found for n-butanol.

The specific activity of the catalysts is about 10% lower than for dehydration of ethanol, but the ratio of activities of the two catalysts is about the same as before; this finding is in complete agreement with our hypotheses. The chief difference is that the dehydrogenation reaction is more in evidence in the case of n-butanol.

Experiments conducted under similar conditions with n-pentanol showed that practically no gaseous dehydration products were obtained with catalyst No. 1; catalyst No. 3 showed a small activity, which fell to zero after a few minutes. Both catalysts were blackened by soot formed from the n-pentanol. Catalyst No. 3 was slightly more active at 400° (35 ml of C_5H_{10} per ml of alcohol) than at 325°. Passage of n-butanol immediately after n-pentanol has been passed shows that dehydration of the former alcohol proceeds at a satisfactory speed (90 ml of C_4H_8 per ml of butanol), showing that the catalyst has retained its activity towards butanol, in spite of its surface being covered with soot formed from the pentanol previously passed over it. These experiments show that the difference in the action of the catalysts on these two alcohols depends on the dimensions of their molecules, and is connected with the size of the pores of the catalyst. The smaller molecule of butanol penetrates into the pores, whereas the pentanol molecule reacts only with the external, geometrical surface of the catalyst, the negligible dimensions of which determine the very low activity of the catalyst in the reaction of dehydration of pentanol. Our findings show that the catalysts have a very large surface and very fine pores, and that a large proportion of the pores do not admit the larger molecules, as the mol. wt. rises, from ethanol to pentanol. It follows further from the smaller activity of catalysts No. 1 and 2 than of 3 for dehydration of ethanol that some of the micro-pores do not admit even these relatively small molecules. A sharply defined activity threshold, corresponding with a Gaussian distribution of pore diameters, occurs for n-pentanol, whereas ethanol and n-butanol molecules correspond with the middle part of the curve.

TABLE 7

Catalyst No.	Total volume of gaseous products, in ml	Volume of products in ml			
		C_4H_8	H_2	CO	CO_2
1	80.1	70.0	4.5	2.4	2.5
3	162.8	139.0	11.7	4.4	1.7

It is known that dehydration of higher alcohols takes place quite satisfactorily at a number of Al_2O_3 preparations (in particular from bauxites). This in no way conflicts with our findings, since it only shows that these catalysts possess micro-pores of large diameter.

Our experiments also confirm that such methods should be used for measuring the surface of catalysts as apply not to the total surface (from nitrogen adsorption) but to the effective active surface, i.e., to that part of the surface which is accessible to the given substrate molecules, but not to the surface of the micro-pores to which the reacting molecules have no access.

SUMMARY

A study of dehydration of HCOOH, ethanol, n-butanol, and n-pentanol at Al_2O_3 catalysts prepared from sedimentation fractions of hydroxide leads to the following conclusions:

1. The activity of catalysts prepared from different hydroxide fractions varies, the most active being catalyst No. 3, obtained from the most coarse-grained hydroxide fraction.

2. X-Ray structural analysis shows that the catalysts are all crystalline, consisting of γ-Al_2O_3 with uniform lattice constants, and not containing any other forms of Al_2O_3 or of its crystal hydrates; their residual water content appears to be in the adsorbed state. The linear dimensions of the crystallites of γ-Al_2O_3 are greatest (51-52 A) for catalyst No. 3, and smallest ($\leq$ 35 A) for catalyst No. 1, prepared from the most highly disperse hydroxide fraction.

3. The derivation of the specific surface from measurements of adsorption of methanol is unsatisfactory, inasmuch as identical values (286 sq.m. per g) were obtained for all three specimens of γ-Al_2O_3, whereas data for adsorption of n-pentane show that they have different surfaces. Catalyst No. 3, the grains of which are made up of the largest crystallites of γ-Al_2O_3 (51 A), has a specific surface of 264 sq. m. per g, as derived from n-pentane adsorption, whereas catalysts No. 1 and 2, which are made up of smaller crystallites, have a specific surface of 182 and 179 sq. m. per g., respectively.

4. It follows from the findings that (a) a catalyst, the grains of which are made up of larger particles, has a bigger surface and a greater activity than one made up of smaller particles, and (b) the specific surface derived from adsorption of smaller molecules (methanol) is greater than with larger molecules of n-pentane, that:

(I) The dimensions of the micro-pores of the catalysts are determined by the size of the elementary crystallites and by the way in which they are packed to give secondary particles (catalyst grains). The optimum dimensions of the crystallites are those which when aggregated into secondary particles give pore dimensions commensurate with the size of the reacting molecules. A scheme is advanced, explaining the effect of this structural factor, and also the existence of an optimum of dispersity.

(II) The estimation of the specific surface of catalysts of organic reactions from low temperature adsorption of nitrogen molecules is unsatisfactory, in view of their small size, and cannot serve as a criterion of the relative activity of different catalysts.

5. The hypotheses advanced in paragraph 4 have been confirmed experimentally, for the cases of dehydration of substances having molecules of widely different size (HCOOH, ethanol, n-butanol, n-pentanol).

6. The concept of effective specific surface has been introduced, in connection with the above findings.

Received April 10, 1951

Institute of Organic Chemistry
Academy of Sciences USSR

LITERATURE CITED

[1] D. N. Vaskevich. Bull. USSR Acad. Sci., Div. Chem. Sci. 3, 325 (1946).

[2] R. Brill, Ergebn. d. Techn. Rontgenkunde, II, 115, 1931.

[3] M. M. Dubinin. "Methods of Study of Catalysts", p. 213. USSR Acad.Sci.Press, [illegible], Moscow-Leningrad, 1948.

[4] A. V. Kiselev, ibid., p. 230.

[5] Harries and P. Emmet, J. Phys. Coll. Chem. 53, 811 (1949).

[6] N. N. Avgul, O. M. Dzhigit, V. P. Dreving, Ya. V. Guriev, A. V. Kiselev, and O.A Likhacheva. Proc. USSR Acad. Sci. 77, 77 (1951).

[7] H. E. Ries, M. Johnson and J. Malik, J. Phys. Coll. Chem. 53, 638 (1949).

[8] A. M. Rubinshtein. Bull. USSR Acad. Sci., Div. Chem. Sci. 4, 815 (1938); A. M. Rubinshtein and N. A. Pribytkova. ibid., 5, 509 (1945).

[9] A. M. Rubinshtein. ibid., 1, 144 (1940); 6, 427 (1943).

[10] A. M. Rubinshtein. ibid., 1, 135 (1940).

[11] S. Z. Roginsky. J. Phys. Chem., 15, 6, 715 (1941); "Adsorption and Catalysis at Heterogeneous Surfaces", p. 24. USSR Acad.Sci.Press, Moscow-Leningrad, 1948. [illegible]

[12] R. Fricke, H. Diefel, Ber. 72, 1568 (1939).

OPTICAL ACTIVITY OF CELLULOSE TRIACETATE

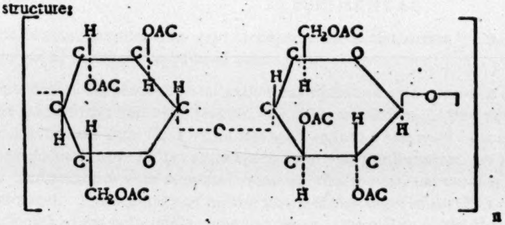
N. M. Bazhenov and M. V. Volkenshtein

Intramolecular interferometry – a study of optical activity – is one of the most valuable methods available to us for the study of intramolecular changes and reactions. The profound ideas of the theory of the structure of organic compounds and of the mutual effects exerted by their constituent atoms, formulated by Butlerov and Markovnikov, were successfully developed by Chugaev, who applied the study of optical activity to the analysis of intramolecular reactions in complex organic substances [1]. The present paper deals with the application of the effect of temperature on optical activity to the study of internal rotations in cellulose triacetate and in simpler compounds of analogous structure.

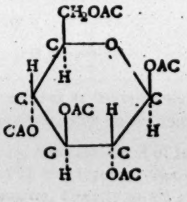
Internal rotation about single bonds in molecules leads to a change in their configuration. The magnitude of the optical rotating power is directly dependent on the geometrical distribution of atoms in the molecule. If the molecule has a low degree of symmetry (axes of symmetry not more than the second order) the possibility of internal rotations leads to the phenomenon of rotational isomerism [2]. Change in temperature leads to change in the relative amounts of the rotational isomers in the mixture, the equilibrium constant of which is thus modified.

Since each rotational isomer of an asymmetric molecule possesses a characteristic optical activity, the value found for the latter should vary with temperature. Differences in the energy of rotational isomers may be derived from the temperature coefficients of optical activity [3]. Only a very few researches on this subject have so far been published, such as on the esters of tartaric acid [4] and on sec-butanol [5].

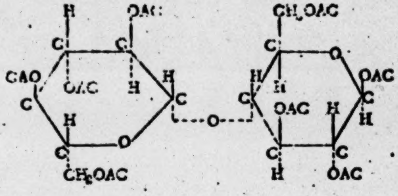
The more important properties of linear polymers are connected with processes of internal rotation. According to the concepts developed by us linear polymers should be regarded as equilibrium mixtures of rotational isomers [6]. We unfortunately know of no optically active, flexible, rubber-like polymers. The present paper is devoted to a polarimetric study of internal rotation in the highly optically active polymer cellulose triacetate. This has the structure:



The properties of the chain as a whole are determined by the rotations relatively to each other of its component links, rotations around C–O bonds linking six-membered rings. Rotations around single bonds in the acetyl side groups are also possible. In order to study separately the effect of these and of other rotations on optical activity, research was done on an analog of a single link of the chain, α-penta-acetyl-d-glucose:



and of the analog of the pair of links, α-octa-acetylcellobiose:



In the former case rotation is possible only in the side-chains, while in the latter rotation is additionally possible around the C–O bond joining the rings.

The greatest difficulty of the research consists in eliminating intermolecular reactions, which would also complicate the effects of temperature on optical rotation. The following relation is derived, on theoretical grounds, between the value of optical rotation and the properties of the solution [7]:

$$\Omega = \frac{[\alpha]}{n^2 + 2} = \Omega_0 + B\,\frac{\epsilon - 1}{\epsilon + 2}, \qquad (1)$$

where $[\alpha]$ is the specific rotation, n is the refractive index, ϵ is the dielectric constant, and Ω and B are constants; Ω and Ω_0 are termed "rotivity".

Since n and ϵ depend on temperature, it follows that Ω must also be a function of temperature T. The functional dependence of molecular rotivity Ω, which represents optical rotatory power in absence of solvent factors, can be considered in isolation if the value of the constant B, and the dependence of n and ϵ on temperature, are known; this involves studies of substances in solvents of widely different n and ϵ.

Formula (1) is not applicable to solutions in which association may take place. We selected triacetylcellulose for our study, since the cellulose is practically completely esterfied, as a result of which association due to formation of hydrogen bridges arising from hydroxyl groups is excluded.

EXPERIMENTAL

The following measurements were made, in order to determine the dependence on temperature of $[\alpha]$, n and ϵ in solutions of the above-mentioned substances:

1. Rotation of the plane of polarization was measured by means of a polarimeter, set up as shown in Fig.1. Readings were taken with three wave lengths, 435, 589, and 656 mμ. The source of light was an electric glow-lamp (12V and 50W), the light from which was split up into a spectrum by means of a monochromator UM-2. The temperature range was from −10° (in some cases, from −40°) to temperatures close to those of the boiling point of the solvents. Temperatures were regulated in an ultrathermostat, not varying by more than 0.1° during the period of the measurement. The accuracy of measurement of the angle of rotation of the plane of polarized light was ±0.02°. The length of the polarimeter tube was 20 cm. Even flow of the thermostat liquid (water and methanol) over the tube was assured. Dimming of the end pieces of the tubes at low temperatures was prevented by fitting protective caps with warmed windows, passing dry air through the caps.

2. At the same time, in order to take into account thermal expansion of the solution, its density was measured by means of a cathetometer, with an accuracy of up to the fourth place.

3. In order to determine rotivity

$$\Omega = \frac{[\alpha]}{n^2 + 2}$$

it is necessary to measure the refractive index at the same temperatures and wave lengths. These measurements were conducted with an IRF-23 refractometer, with an accuracy of $\pm 2\cdot 10^{-4}$.

4. Measurement of the dielectric constant ϵ and of its temperature coefficient were made with the aid of the Q-meter KV-1, at a frequency of 11 megacycles. The measuring condenser, shown schematically in Fig.2, is connected, together with the thermometer, directly to the efferent terminals of the Q-meter, thus greatly lowering the effect of scattered capacity. The temperature of all the instruments was maintained by means of

one and the same ultrathermostat.

Triacetylcellulose with an equivalent acetic acid content of 62.5% was purified by precipitation with ethanol from filtered solutions in the appropriate solvent. The concentration varied according to the solvent, from 0.01 to 0.05 g per ml of solvent; experiment showed that specific rotation [α] does not depend on concentration within these limits.

α-Penta-acetylglucose was prepared in our laboratory by scientific worker Sogomonyants by acetylation of glucose, by the standard method [8]. It melted at 110-111° (published m.p. 110-113°; $[\alpha]^{20}$, 101.6°, in chloroform). α-Octa-acetylcellobiose was also prepared by Sogomonyants, by a standard method [9], m.p. 224-225° (published m.p. 225-226°; $[\alpha]^{20}_{D}$ 42.5°, in chloroform).

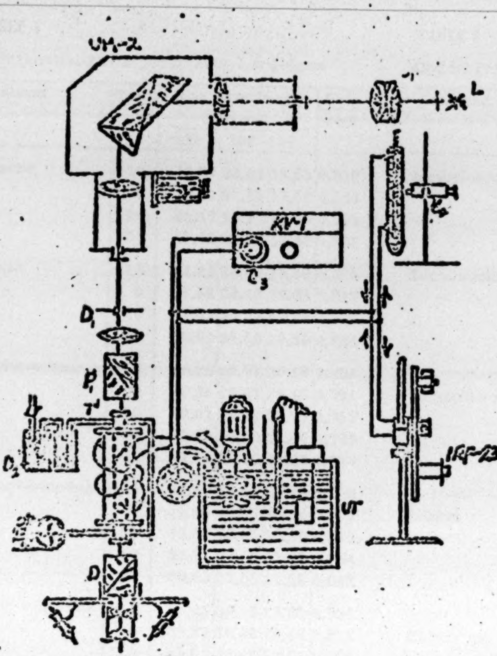


Fig. 1. Polarimeter scheme: UM-2) monochromator, C1) condenser; L) lamp; D) diaphragm; P_1) two-field polarizer; D_1) drier; T) tube; P_2) pump; A) analyzer; UT) ultrathermostat; C_2) cathetometer; KV-1) Q-meter; C_3) condenser; IRF-23) refractometer; [illegible] CA): cold accumulator.

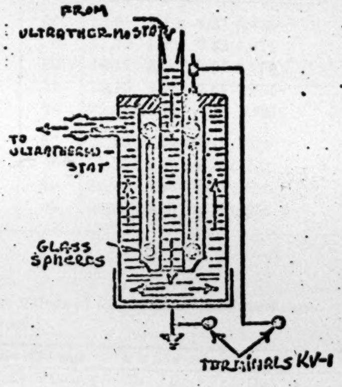


Fig. 2. Measuring condenser.

Expression (1) gives a linear relation between the Ω of a substance and the value of $(\epsilon-1)/(\epsilon+2)$, at a given temperature. The values of Ω obtained by us give a certain scatter about the straight line expected for the $\Omega-(\epsilon-1)/(\epsilon+2)$ curve; this is not unnatural, if we take into account the simplifying assumptions made in the derivation of the initial formula (cf. [7]). Our case is one of a solution of a polar substance in polar solvents. We can, nevertheless, consider the curve $\Omega-(\epsilon-1)/(\epsilon+2)$ to be roughly rectilinear, and we may make use of it to determine the values of the constants B and Ω_0. We applied the method of smallest squares for selection of the most probable curve. We thus arrived at the values of Ω_0 and B, as functions of temperature. The values of Ω_0 (T) found experimentally, and calculated are given in Table 4.

DISCUSSION OF RESULTS

All three substances exhibit a noticeable dependence of real specific rotivity Ω_0 on temperature, which cannot be referred to the action of the solvent; this is evidence of the presence of internal rotations in these substances. In order to determine the nature of these internal rotations it is necessary to compare the temperature dependence of rotivity of triacetylcellulose with those of the monomer and dimer. The following possibilities may exist:

TABLE 1

Optical Activity of α penta-Acetyl d-glucose

Solvent	Temp. °C	Ω at wave lengths in mμ			$\frac{\epsilon-1}{\epsilon+2}$
		435	589	656	
Benzene	−10	40.77	23.04	17.51	0.312
	0	40.91	23.11	17.57	0.307
	20	41.10	23.28	17.69	0.301
	50	41.62	23.52	17.86	0.291
Dioxan	−10	31.40	24.66	19.56	0.328
	0	31.52	24.48	19.63	0.317
	20	31.72	24.33	19.75	0.299
	50	32.70	25.50	20.89	0.284
Dichloroethane	−10	49.24	25.71	20.18	0.793
	0	49.66	25.87	20.40	0.781
	20	50.02	26.18	20.77	0.757
	50	50.79	26.70	21.44	0.720
	70	51.15	26.90	21.84	0.694
Tetrachloroethane	−10	49.20	25.85	20.48	0.728
	0	49.35	25.98	20.54	0.715
	20	49.87	26.31	20.79	0.686
	50	50.32	26.60	21.12	0.634
	70	50.63	27.05	21.38	0.603
Acetic anhydride	−10	55.23	30.10	23.43	0.894
	0	55.38	30.30	23.49	0.831
	20	55.67	30.40	23.64	0.873
	50	56.14	30.80	23.83	0.860
	70	56.46	30.90	23.99	0.850

TABLE 2

Optical Properties of α octa-Acetylcellobiose

Solvent	Temp. °C	Ω at wave lengths in mμ			$\frac{\epsilon-1}{\epsilon+2}$
		435	589	656	
Methylenechloride	−10	21.99	12.18	9.41	0.753
	0	22.17	12.28	9.54	0.740
	20	22.56	12.46	9.77	0.716
	40	22.91	12.65	9.97	0.693
Dichloroethane	−10	22.83	12.30	9.75	0.793
	0	22.83	12.29	9.74	0.781
	20	22.92	12.33	9.75	0.757
	50	23.06	12.36	9.73	0.720
	70	23.15	12.39	9.72	0.694
Tetrachloroethane	−10	18.28	10.03	8.00	0.728
	0	18.29	10.02	7.98	0.715
	20	18.35	10.06	8.01	0.686
	50	18.40	10.07	7.97	0.634
	70	18.44	10.09	7.95	0.603
Dioxan	−10	18.61	9.10	7.21	0.328
	0	18.79	9.22	7.33	0.317
	20	19.15	9.50	7.60	0.299
	50	19.69	9.86	7.96	0.284
	70	20.06	10.12	8.23	0.281
Chloroform	−10	21.54	11.52	10.61	0.610
	0	21.33	11.28	10.45	0.581
	20	20.91	10.84	10.09	0.550
	50	20.32	10.03	9.56	0.515

TABLE 3

Optical Properties of Triacetylcellulose

Solvent	Temp. °C	Ω at wave lengths in mμ			$\frac{\epsilon-1}{\epsilon+2}$
		435	589	656	
Nitromethane	−10	−3.00	+0.68	+1.27	0.931
	0	−3.39	+0.33	+0.92	0.926
	20	−4.23	−0.41	+0.26	0.917
	50	−5.40	−1.55	−0.72	0.909
	70	−6.20	−2.29	−1.41	0.896
Tetrachloroethane	−10	−7.11	−2.87	−2.12	0.728
	0	−7.46	−3.21	−2.36	0.715
	20	−8.18	−3.84	−2.95	0.686
	50	−9.20	−4.79	−3.74	0.634
	70	−10.00	−5.31	−4.25	0.603
Chloroform	−10	−9.40	−4.93	−3.73	0.610
	0	−9.63	−5.15	−3.79	0.581
	20	−10.00	−5.50	−4.11	0.550
	50	−10.50	−6.03	−4.61	0.515

TABLE 4

Comparison of the Values of Ω_0 (T), Obtained Experimentally and Calculated

Substance	Temp. °C	λ = 435 mμ		λ = 589 mμ		λ = 656 mμ	
		Ω_0	$\Omega_{calc.}$	Ω_0	$\Omega_{calc.}$	Ω_0	$\Omega_{calc.}$
α-Penta-acetyl-glucose	−10	22.59	22.20	18.76	18.65	14.49	14.50
	0	22.95	22.95	18.85	18.95	14.71	14.68
	20	23.74	24.20	19.45	19.45	15.07	15.08
	50	25.42	25.70	20.01	20.01	15.44	15.44
	70	27.17	26.45	–	20.28	–	15.52
α-Octa-acetyl-cellobiose	−10	8.23	8.20	3.38	3.44	0.72	0.60
	0	8.41	8.41	3.83	3.91	1.11	1.38
	20	8.77	8.75	4.87	4.65	2.55	2.55
	50	9.12	9.08	5.31	5.38	3.67	3.67
	70	–	9.22	–	5.70	–	4.15
Tri-acetyl-cellulose	−10	−21.52	−21.35	−15.52	−15.18	−13.34	−13.00
	0	−20.33	−20.42	−14.54	−14.45	−12.01	−12.28
	20	−18.83	−18.95	−13.25	−13.27	−10.94	−11.12
	50	−17.44	−17.47	−12.00	−12.06	−9.96	−9.97
	70	−16.81	−16.81	−11.49	−11.52	−9.49	−9.46

(a) The $\Omega(T)$ curve for triacetylcellulose is characterized by parameters which differ radically from those characterizing the corresponding curves for the monomer and dimer. In that case, the difference may be ascribed to rotations of individual links of the chain; in this case the $\Omega(T)$ curves for the dimer and the monomer should be radically different.

(b) All three $\Omega(T)$ curves have parameters which differ little from each other. In this case the effect of temperature is confined to rotation of the side acetyl groups, since there can be no question of rotation of the ring.

We attempted to describe all three curves by means of an empirical equation of the type

$$\Omega(T) = \frac{\Omega^{(1)} + \Omega^{(2)} A e^{-\frac{E}{RT}}}{1 + A e^{-\frac{E}{RT}}}, \qquad (2)$$

where $\Omega^{(1)}$, $\Omega^{(2)}$, A and E are constants, determined experimentally, R is the gas constant, and T is absolute temperature. The constants $\Omega^{(1)}$, $\Omega^{(2)}$, A, and E are determined in the following way. Let

$$x_1 = -\frac{E}{RT_1},$$

then

$$\Omega_1 = \frac{\Omega^{(1)} + \Omega^{(2)} A e^{x_1}}{1 + A e^{x_1}} \qquad (3)$$

Taking $\Omega^{(1)}(x_1)$ equations for four temperatures, and eliminating $\Omega^{(1)}$ and $\Omega^{(2)}$, we obtain two expressions for A:

$$A = \frac{(\Omega_1 - \Omega_2)(e^{x_2} - e^{x_3}) - (\Omega_2 - \Omega_3)(e^{x_1} - e^{x_2})}{(\Omega_2 e^{x_2} - \Omega_1 e^{x_1})(e^{x_2} - e^{x_3}) - (\Omega_3 e^{x_3} - \Omega_2 e^{x_2})(e^{x_1} - e^{x_2})}$$

and

$$A = \frac{(\Omega_2 - \Omega_3)(e^{x_3} - e^{x_4}) - (\Omega_3 - \Omega_4)(e^{x_2} - e^{x_3})}{(\Omega_3 e^{x_3} - \Omega_2 e^{x_2})(e^{x_3} - e^{x_4}) - (\Omega_4 e^{x_4} - \Omega_3 e^{x_3})(e^{x_2} - e^{x_3})}.$$

We find graphically at which values of E these equations give the same value of A. We find $\Omega^{(1)}$ and $\Omega^{(2)}$ by a reverse substitution. The results so obtained are given in Table 5 (compare with Table 4). A comparison of experimental and calculated values of Ω for λ = 589 mμ is given in Figure 3.

TABLE 5

Parameters Characterizing Rotivity of the Substances Studied

λ in mμ	E cal/mol.	A	$\Omega^{(1)}$	$\Omega^{(2)}$
	Triacetylcellulose			
435	2800	445	−37.03	−14.11
589	3000	500	−24.79	−9.42
656	3000	591	−23.74	−7.55
Mean	2900	512	—	—
	α-Octa-acetylcellobiose			
435	3200	836	5.30	9.72
589	3200	814	−2.80	6.80
656	2800	722	−18.43	6.00
Mean	3100	791	—	—
	α-Penta-acetylglucose			
435	3000	300	14.80	29.60
589	2800	234	15.37	21.52
656	2800	336	11.49	16.34
Mean	2900	290	—	—

Agreement of the same order is obtained using other wave lengths.

Thus the temperature dependence of Ω differs little for the three substances studied. The important constant E has practically the same value in all three cases. It is of interest that the value of the constant A for triacetylcellulose is intermediate between the values for penta-acetylglucose and octa-acetylcellobiose.

Equation (2) is an empirical one, but it has a definite physical significance. Let us imagine an equilibrium mixture of two rotational isomers 1 and 2, with rotivities $\Omega^{(1)}$ and $\Omega^{(2)}$. The rotivity of the mixture is given by

$$\Omega = \frac{1}{N}\left(N_1 \Omega^{(1)} + N_2 \Omega^{(2)}\right), \qquad (4)$$

where $N = N_1 + N_2$, and is the total number of molecules per unit volume, N_1 and N_2 being the number of molecules of isomers 1 and 2, respectively. The ratio $N_1 : N_2$ is determined by the difference in the energies E of the isomers

$$\frac{N_2}{N_1} = A e^{-\frac{E}{RT}}, \qquad (5)$$

where A is the ratio of statistical weights of isomers 2 and 1.

Substituting in equations (5) and (4) we obtain Equation (2).

The number of different rotational isomers of our substances must in practice be very great indeed, in view of the large number of groups capable of rotation present in the molecule, and for this reason our empirical equation has no direct theoretical significance. This is also indicated by the large values of A, as in reality the ratios of the statistical weights of the rotational isomers should be hundreds of times smaller. The values of E determined by us do, however, have a physical meaning, if only for giving the order of magnitude characteristic of the mean differences in the energies of rotational isomers. The usual value for the energy of rotation around single bonds is 3 kcal; this is the value of the potential barrier in the case of ethane.

We have thus found that internal rotations of the same type take place in all three substances — monomer, dimer, and polymer. These must obviously be rotations of the acetyl side chains; we were not able to find evidence for rotation of the rings relatively to each other, and this is in accordance with the known rigidity of the cellulose chain.

It is known that a certain freedom of rotation of side-chains of polymers is indicated by their specific electrical properties [10], and in other ways. Our findings show that the study of the dependence of optical activity on temperature provides a new and valuable method of investigating these important processes.

We express our sincere gratitude to Zh. S. Sogomonyants, a scientific worker of our laboratory, for preparing and purifying the substances and solutions used in our research.

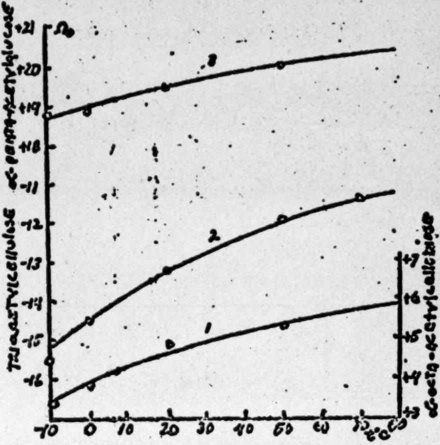


Fig. 3. Curves connecting rotivity with temperature for α-octa-acetylcellobiose, triacetylcellulose, and α-penta-acetylglucose. 1) $\Delta E = 2800$ cal/mol.; $A = 234$; $\Omega^{(1)} = 15.37$; $\Omega^{(2)} = 21.52$; 2) $\Delta E = 3000$ cal/mol.; $A = 500$; $\Omega^{(1)} = -24.79$; $\Omega^{(2)} = -9.42$; 3) $\Delta E = 2800$ cal/mol.; $A = 234$; $\Omega^{(1)} = 15.37$; $\Omega^{(1)} = 21.52$. The curves satisfy the equation

$$\Omega_0 = \frac{\Omega^{(1)} + \Omega^{(2)} A e^{-\frac{\Delta E}{RT}}}{1 + A e^{-\frac{\Delta E}{RT}}}.$$

The small circles represent experimental values of Ω_0.

SUMMARY

The dependence of optical activity on temperature has been studied for triacetylcellulose, α-penta-acetylglucose, and α-octa-acetylcellobiose, in various solvents, and over a wide range of temperatures and wave lengths. It was found that in all three cases internal rotation of the acetyl side-chains of the molecules took place, but that rotation relative to each other of the constituent rings of the chains did not take place.

LITERATURE CITED

[1] M.V.Volkenshtein and A.M.Efros. Prog. Chem., istry, 19, 602 (1950).
[2] M.V.Volkenshtein, M.A.Elyashevich, and B.I.Stepanov. Oscillations of Molecules, Vol. 2, Ch. 28 (1949).
[3] M.V.Volkenshtein. Bull.Acad.Sci.USSR, Phys. Ser., 14, 4 (1950).
[4] F.Winther. Z. phys. Chem., 41, 161 (1902).
[5] H. Bernstein and E. Pedersen. J. Chem. Phys., 17, 885 (1949).
[6] M.V.Volkenshtein. Proc. Acad. Sci., USSR, 78, 5, 879 (1951).
[7] C. Beckmann and K. Cohen. J. Chem. Phys., 4, 784 (1936).
[8] H. Behrend and A. Roth. Ann., 331, 361 (1904).
[9] Syntheses of Organic Compounds, 5, p. 67 (1938).
[10] A.P.Aleksandrov, P.P.Kobeko, and E.V.Kuvshinsky. J.Tech.Phys., 6, 1311 (1936); P.P.Kobeko, G.P.Mikhailov, and Z.P.Novikova. J. Tech.Phys., 14, 1 (1944); 19, 1 (1949).

Received October 12, 1951

Institute of High-Molecular Compounds, USSR Academy of Sciences

REACTIONS OF DIENE HYDROCARBONS WITH NITROSO-COMPOUNDS. ADDITION OF BUTA-1,3-DIENE TO NITROSOBENZENE

PART 1.

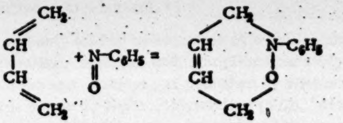
Yu. A. Arbuzov

Nesmeyanov and Ioffe in 1941 isolated from the dark brown tarry product of reaction of p-nitrosodimethylaniline with buta-1,3-diene a small amount of a golden yellow crystalline substance, $C_{12}H_{14}N_2$, m.p. 138-139°, by the method of chromatographic adsorption. In 1945 Nesmeyanov and Khrulev found that nitrosobenzene and buta-1,3-diene, at or slightly above room temperature, give a colorless crystalline product, m.p. 49.5-50°, in good yield. Elementary analysis of this product gives the formulas, $C_{10}H_9ON$ or $C_{10}H_{11}ON$.

I have found that buta-1,3-diene reacts smoothly with nitrosobenzene at 0°, giving a product, $C_{10}H_{11}ON$, m.p. 50-51°. The reaction thus consists in addition of 1 mol of buta-1,3-diene to 1 mol of nitrosobenzene. In my first experiments nitrosobenzene was left in a sealed tube with excess of butadiene for a number of days at 5-10°, until the reaction was completed, when the tubes were opened, excess butadiene was evaporated off, and the residue was recrystallized from light petroleum, and then from ethanol; yield of product of m.p. 50-51°–60% of theoretical. When this same reaction was repeated on a larger scale, however, taking 32.1 g of nitrosobenzene, the temperature of the reaction mixture rose, until the reaction ended in a violent explosion; for this reason, later experiments were conducted with cooling by means of ice. The reagents were kept in a sealed tube in an ice bath for a week, the tube was opened, excess of butadiene was evaporated off, and the residue was steam-distilled, giving a 90% yield of addition product. Subsequent experiments were conducted at 0°, diluting the reagents with various solvents (ethanol, ether, chloroform). Butadiene was added to solutions of nitrosobenzene in the solvents at 0°, the flask was left in the ice bath for 1-2 days, the solvent was distilled off, and the residue was distilled in vacuum; the yield of addition product was 90-95 %.

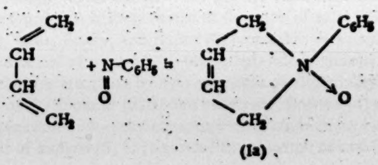
The addition product is readily soluble in warm light petroleum, cyclohexane, methanol, and ethanol, and in cold chloroform and acetic acid; it is practically insoluble in water. It can be steam-distilled or vacuum distilled (b.p. 107-108°/3.5 mm) without decomposition. It is hydrolyzed when heated with dilute mineral acids (10% sulfuric or 5% hydrochloric acid).

We could, on theoretical grounds, envisage two ways in which addition could take place. If the reaction proceeds as a diene synthesis the product should be 2-phenyl-3,6-dihydro-ortho-oxazine (I):



(I)

If butadiene adds on at the 1,4 positions to the nitrosobenzene nitrogen atom the product should be the N-oxide of 1-phenyl-2,5-dihydropyrrole (Ia):



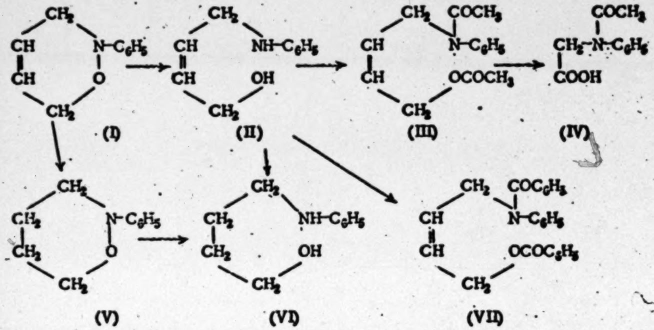
(Ia).

We know that sulfur dioxide reacts similarly with dienes.

The physical properties of the addition product (insolubility in water, solubility in hydrocarbons, volatility in steam, etc.) are not compatible with structure (Ia). The remaining alternative is therefore that the reaction of butadiene with nitrosobenzene proceeds according to the diene synthesis, and that the product must be 2-phenyl-3,6-dihydro-ortho-oxazine (I). An examination of the structure of the addition product confirmed this supposition.

Structure (I) for the addition product was established in the following way. Reduction of the addition product with zinc dust and acetic acid gave 4-anilinobut-2-en-1-ol (II), identified as the dibenzoyl derivative (VII) (m.p. 90-91°). Acetylation of 4-anilino-but-2-en-1-ol (II) with acetic anhydride gave the diacetyl derivative (III), oxidation of which with potassium permanganate in acetone gave N-acetyl-N-phenylglycine (IV).

The catalytic hydrogenation of 2-phenyl-3,6-dihydro-ortho-oxazine and 4-anilinobut-2-en-1-ol was next studied.



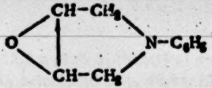
Catalytic hydrogenation of 2-phenyl-3,6-dihydro-ortho-oxazine (I) in presence of platinized charcoal gives 2-phenyltetrahydro-ortho-oxazine (V), which is reduced by zinc dust and acetic acid to 4-anilinobutan-1-ol (VI).

Catalytic reduction of 4-anilinobut-2-en-1-ol (II) should give 4-anilinobutan-1-ol (VI), but with platinized charcoal about 1.8 mol of hydrogen was absorbed per mol of 4-anilinobut-2-en-1-ol (II), giving a reaction product which boiled over a wide range of temperatures, and from which were isolated n-butanol, aniline, N-n-butylaniline, and 4-anilinobutan-1-ol (VI), obtained in only 17% yield, the basic products being butanol and aniline. These are produced probably by hydrogenolytic fission of 4-anilinobut-2-en-1-ol at the N-allyl bond, giving aniline and but-2-en-1-ol, which is further reduced to n-butanol.*

N-n-Butylaniline is probably formed by reduction of 4-anilinobut-2-en-1-ol to but-2-enylaniline, which is further reduced to N-n-butylaniline. After we had completed our study of the product of addition of butadiene to nitrosobenzene a paper on the same subject was published by Wichterle [6], who, however, came to the mistaken conclusion that it is 3,4-oxido-N-phenylpyrrolidine (VIII). After I had published my paper [7] Wichterle [8] admitted that he was wrong, and that the structure of the addition product given by me as structure (I) is the correct one.

---

* The reaction of hydrogenolytic fission at the N-allyl bond has been described in the literature. Thus Kleinschmidt and Cope [1] found that hydrogenation in presence of palladized charcoal of crotylmethylaniline gives methylaniline. Cope, Estes, Emery, and Haven [2] found that dimethylamine is formed by hydrogenation in presence of palladized norite of trans-1,2-bis-(dimethylamino)-cyclopent-3-ene. Emde and Kull [3] showed that trialkylamine hydrochlorides are given by hydrogenation of allyltrialkylammonium or cinnamyltrialkylammonium chlorides in presence of platinum or palladium catalysts. Howton [4] showed that trimethylamine hydrobromide is obtained by hydrogenation of 2-cyclohexenyltrimethylammonium bromide in presence of platinum, nickel, or palladium. A number of authors [5] have studied the reaction of catalytic debenzylation of N-benzylamines.



(VIII)

EXPERIMENTAL

Preparation of 2-phenyl-3,6-dihydro-ortho-oxazine

Experiment 1. 10.7 g (0.1 mole) of nitrosobenzene and 10.7 g of butadiene were placed in a tube which was cooled in a mixture of solid carbon dioxide and ethanol. The tube was sealed and left for 24 hours at 5-10° in a water bath. The tube was shaken from time to time during the first 5 hours, and the whole of the nitrosobenzene had passed into solution at the end of 6 hours. After 24 hours the originally green solution had become light brown, and light brown crystals had formed on the walls of the tube. The tube was cooled, opened, and unreacted butadiene was allowed to evaporate off. The residue was recrystallized from 30 ml of light petroleum, the hot solution being filtered, leaving about 0.6 g of an insoluble, yellow, finely crystalline substance, m.p. 181-184° (decomposition). Light yellow crystals were deposited by the cooled solution, and these were collected and washed with light petroleum. After two recrystallizations from 15 ml of ethanol a yield of 9.0 g (61% of theoretical) of a colorless, finely crystalline substance, m.p. 50-51°, was obtained.

Found %: C 74.70; 74.98; H 6.69; 6.63; N 8.72; 8.78

$C_{10}H_{11}ON$. Calculated %: C 74.50; H 6.88; N 8.69.

Experiment 2. A tube containing 10.7 g (0.1 mole) of nitrosobenzene and 21.4 g of butadiene was placed in an ice bath for a week, the tube shaken every 12 hours during the first 3 days. The tube was opened after 7 days, excess butadiene evaporated off, and the residue steam distilled. The crystalline product appearing in the distillate was collected and dried in a desiccator over H_2SO_4, giving 14.8 g (91% yield) of 2-phenyl-3,6-dihydro-ortho-oxazine, m.p. 49-50°. The light yellow product was recrystallized from ethanol; colorless product, m.p. 50-51°.

Found %: C 74.80; 74.84; H 6.83; 6.87; N 8.63; 8.61

$C_{10}H_{11}ON$. Calculated %: C 74.50; H 6.88; N 8.69

Experiment 3: 28 g of butadiene was introduced into a flask containing 26.8 g (0.25 mole) of nitrosobenzene, at 0°, and the flask was left on ice for some days, after which the solvent was distilled off, and the residue was vacuum distilled, giving 36.4 g (90% of theoretical) of 2-phenyl-3,6-dihydro-ortho-oxazine, b.p. 107-108° at 35 mm, affording colorless crystals, m.p. 50-51°, after recrystallization from ethanol.

Experiment 4. 28 g of butadiene was placed in a flask containing 26.8 g (0.25 mole) of nitrosobenzene in 500 ml of ether, at 0°. Two days later the ether was distilled off, and the residue was distilled in vacuum, giving 36.5 g (91% of theoretical) of 2-phenyl-3,6-dihydro-ortho-oxazine, b.p. 108-109° at 4 mm, m.p. after recrystallization from ethanol 50-51°.

Experiment 5. 110 g butadiene was added to 107.1 g (1 mole) nitrosobenzene in 1 liter chloroform, at 0°. The chloroform was distilled off after a few days at 0°, the residue distilled in vacuum, giving 154.0 g (95% of theoretical) of 2-phenyl-3,6-dihydro-ortho-oxazine, b.p. 108-109° at 4 mm, m.p. 50-51°, after recrystallization from methanol.

Found %: C 74.32; 74.23; H 6.84; 6.87; N 8.59; 8.42

$C_{10}H_{11}ON$. Calculated %: C 74.50; H 6.88 N 8.69

Reduction of 2-phenyl-3,6-dihydro-ortho-oxazine with zinc dust and acetic acid, to give 4-anilinobut-2-en-1-ol

20 g of zinc dust was added to 16.1 g (0.1 mole) of 2-phenyl-3,6-dihydro-ortho-oxazine in 200 ml of glacial acetic acid, in a 450 ml bottle, which was stoppered, and was shaken for 10 min., when a second 20 ml portion of zinc dust was added, followed by shaking for another 10 min.; there was a considerable temperature rise during the first shaking, and a much smaller one during the second. 200 ml of water, followed by 200 g sodium hydroxide, with cooling, were then added, and the mixture was steam distilled, collecting about 500 ml of distillate. The residue in the distilling flask was then filtered hot, and the cooled filtrate was extracted with 5 successive 100 ml portions of benzene. The benzene extract was washed with water[*], the benzene was distilled off, and the residue was

---

[*] The benzene extract should be well washed with water, as it was noticed that thermal decomposition of 4-anilinobut-2-en-1-ol takes place during its vacuum distillation if even traces of caustic alkali are present, giving aniline and tarry products. The following experiment was done, in view of this observation. A few lumps of fused potassium hydroxide were added to a solution of 12.5 g of 4-anilinobut-2-en-1-ol, b.p. 161-162°/4.5 mm, in 30 ml of dry benzene, the solution was filtered after 12 hours, the filtrate was distilled to remove benzene, and the residue was distilled from a metal bath, at 5 mm. Energetic decomposition began when the temperature reached 155°, and a low b.p. distillate, containing tar, was formed; fractionation of the distillate gave 4.3 g of aniline, b.p. 69° at 10 mm; d_4^{20} 1.0193; n_D^{20} 1.5860, identified as acetanilide, m.p. 113.5-114°.

fractionally distilled in vacuum, giving 13.3 g (82% of theory) of 4-anilinobut-2-en-1-ol, b.p. 151-152°/2 mm, d_4^{20} 1.0816; n_D^{20} 1.5867; found MR_D 50.69; calculated MR_D 49.44; EMR_D 1.25. The product is a colorless, viscous liquid, which becomes yellow on storage..

Found %: C 73.56; 73.46; H 8.19; 8.13; N 8.83; 8.98
$C_{10}H_{13}ON$. Calculated %: C 73.59; H 8.03; N 8.58
Found %: [H*] 1.11; 1.11
$C_{10}H_{11}ON[H^*]_2$ Calculated %: [H*] 1.24

Dibenzoyl derivative of 4-anilinobut-2-en-1-ol

Benzoyl chloride (14.1 g; 0.1 mol) was added in 5 portions during 30 min to 4.90 g (0.03 mol) of 4-anilinobut-2-en-1-ol and 60 ml of 10% caustic soda, shaking vigorously after each addition. Excess of benzoyl chloride was hydrolyzed by heating on the water bath, and the crystalline product was collected by filtration, washed with water, and dried in a desiccator over sulfuric acid. A yield of 10.5 g of dibenzoyl derivative of 4-anilinobut-2-en-1-ol, m.p. 87-90°, was obtained (94% of theory); the m.p. was 90-91° after 2 recrystallizations from ethanol.

Found %: C 77.91; 78.01; H 5.78; 5.72; N 3.89; 3.90
$C_{24}H_{21}O_3N$. Calculated %: C 77.61; H 5.70; N 3.77

Diacetyl derivative of 4-anilinobut-2-en-1-ol

A solution of 16.3 g (0.1 mol) of 4-anilinobut-2-en-1-ol in 60 ml of acetic anhydride was heated under reflux on a boiling water bath for 3 hrs, after which acetic acid and excess of acetic anhydride were distilled off under reduced pressure (50 mm), and the residue was distilled at 1 mm, giving 23.2 g (94% of theoretical) of the diacetyl derivative of 4-anilinobut-2-en-1-ol, with the following constants: b.p. 160-161°/ 1 mm; d_4^{20} 1.1053; n_D^{20} 1.5271; found MR_D 68.79; calculated MR_D 68.04*; EMR_D 0.75. The product was a colorless viscous liquid.

Found %: C 67.80; 67.82; H 6.93; 6.86; N 6.04; 6.10
$C_{14}H_{17}O_3N$ Calculated %: C 68.00; H 6.93; N 5.66

Oxidation of the diacetyl derivative of 4-anilinobut-2-en-1-ol to N-acetyl-N-phenylglycine

A solution of 4.7 g (0.03 mol) of potassium permanganate in 350 ml of dry acetone was added with constant stirring during 90 min to 2.47 g (0.01 mol) of the diacetyl derivative of 4-anilinobut-2-en-1-ol in 100 ml of dry acetone. The solution was filtered on the next day, and the deposit was washed with acetone, and extracted with 50 ml of water. The aqueous extract was extracted with chloroform, and was then made acid with hydrochloric acid. The precipitate was collected, washed with cold water, and dried in a desiccator over sulfuric acid; yield 1.20 g (62% of theory) of N-acetyl-N-phenylglycine, m.p. 191-193°, raised to 194-195° after recrystallization from hot water.

Found %: C 62.26; 62.22; H 5.73; 5.72; N 7.17; 7.00
$C_{10}H_{11}O_3N$. Calculated %: C 62.16; H 5.74; N 7.25

A mixture of our product with N-acetyl-N-phenylglycine, m.p. 193-195°, prepared by the method of Bischoff and Hausdoerfer [11], melted at 193.5-195°. Published m.p. data are 190-191° [10] and 194-195° [11].

Catalytic hydrogenation of 2-phenyl-3,6-dihydro-ortho-oxazine to 2-phenyltetrahydro-ortho-oxazine

Hydrogenation of 32.2 g (0.2 mol) of 2-phenyl-3,6-dihydro-ortho-oxazine in 200 ml of cyclohexane was effected at room temperature and atmospheric pressure, in presence of 3 g of platinized charcoal (10% Pt), being completed in 2 hrs, when 4690 ml of hydrogen (at N.T.P.) had been adsorbed. The catalyst was filtered off, and the cyclohexane distilled off, the residue being fractionally distilled in vacuum, giving 25.4 g (78% of theory) of 2-phenyltetrahydro-ortho-oxazine, with the following constants: b.p. 104-105°/4 mm, d_4^{20} 1.0593; n_D^{20} 1.5550; found MR_D 49.45; calculated MR_D 47.80**; EMR_D 1.65. The product was a colorless, fairly mobile liquid, rapidly yellowing on storage.

---

* The value of 2.49 was taken for amide nitrogen, in calculating molecular refraction [9].

** In calculating molecular refraction a value of 2.48 was taken for hydroxylamine nitrogen [12]. Kleinschmidt and Cope [1] showed that β-arylhydroxylamines display exaltation, varying from 1.09 to 1.5.

Found %: C 73.49; 73.48; H 8.04; 8.15; N 8.71; 8.73

$C_{10}H_{13}ON$. Calculated %: C 73.59; H 8.03; N 8.58

Reduction of 2-phenyltetrahydro-ortho-oxazine by zinc dust and acetic acid, to 4-anilinobutan-1-ol

40 g of zinc dust was added in four portions during 20 min to a solution of 16.3 g (0.1 mol) of 2-phenyltetrahydro-ortho-oxazine in 200 ml of glacial acetic acid, in a bottle, which is stoppered and shaken after each addition. A considerable temperature rise was observed after adding the first and second portions of zinc dust, but not with subsequent portions. 200 ml of water, followed by 200 g of sodium hydroxide, with cooling, were added to the reaction mixture, which was then steam-distilled, to remove volatile products, collecting about 500 ml of distillate. The residue in the distilling flask was filtered hot, and the cooled filtrate was extracted with 5 successive portions of benzene. The benzene extract was washed with water, the benzene was distilled off, and the residue was fractionally distilled in vacuum, giving 7.7 g (47% of theory) of 4-anilinobutan-1-ol, with the following constants: b.p. 154-155°/3 mm, d_4^{20} 1.0498; n_D^{20} 1.5636; found MR_D 51.15; calculated MR_D 49.91; EMR 1.24. The product is a viscous colorless liquid, turning yellow on keeping. Published physical data are: b.p. 157°/3 mm; d_4^{20} 1.0508; n_D^{20} 1.5629 [8].

Found %: C 72.77; 72.54; H 9.17; 9.32; N 8.50; 8.59

$C_{10}H_{15}ON$. Calculated %: C 72.69; H 9.15; N 8.48

4-Anilinobut-1-yl hydrogen oxalate

A solution of 0.38 g (0.003 mol) of oxalic acid dihydrate in 2.1 ml of ethanol is added to 0.5 g (0.003 mol) of 4-anilinobutan-1-ol, and the salt separating is collected and washed with ethanol; yield, 0.61 g of acid oxalate, colorless needles, m.p. 124.5-125° (decomposition) (published m.p. 124.8-125° (decomposition) [8]).

Found %: C 56.65; 56.77; H 6.39; 6.64; N 5.51; 5.64;

$C_{12}H_{17}O_5N$. Calculated %: C 56.46; H 6.71; N 5.49

Catalytic hydrogenation of 4-anilinobut-2-en-1-ol

Four experiments on the catalytic hydrogenation of 4-anilinobut-2-en-1-ol at room temperature and ordinary pressure were performed, with platinized charcoal catalyst. For each experiment 8.16 g (0.05 mol) of 4-anilinobut-2-en-1-ol in 70 ml of ether, and 2 g of platinized charcoal (5% Pt) were taken; the results obtained are given in the Table.

TABLE

Expt. No.	Duration of experiment	Ml of hydrogen absorbed, (0°/760 mm)
1	3 hrs.45 min	1990
2	3 " 30 "	1985
3	3 " 15 "	1955
4	3 " 30 "	1985

The catalyzates from all 4 experiments were united, the ether was distilled off, and the residue was fractionally distilled, giving the following products: (a) n-butanol, (b) aniline, (c) N-n-butylaniline, and (d) 4-anilinobutan-1-ol.

(a) n-Butanol (4.72 g) had the following constants: b.p. 116.5-117.5°/742 mm; d_4^{20} 0.8099; n_D^{20} 1.4008. Published values are: b.p. 117.7°/760 mm; d_4^{20} 0.810; n_D^{20} 1.3993 [13].

n-Butanol was further identified by preparing the α-naphthylurethane. A mixture of 1.6 g of the fraction, b.p. 116.5-117.5°/742 mm, and 3.4 g of α-naphthyl isocyanate was heated until reaction commenced, and was then left until the next day. The n-butyl-α-naphthylurethane was twice recrystallized from n-heptane, when it melted at 70.5-71.5°.

Found %: C 74.07; 74.10; H 7.04; 7.02; N 5.68; 5.84

$C_{15}H_{17}O_2N$. Calculated %: C 74.05; H 7.04; N 5.76

The mixed m.p. with n-butyl-α-naphthylurethane prepared from a known sample of pure n-butanol was 70.5-71.5°; published m.p. are 71-72° [14] and 70° [15].

(b) Aniline (8.71 g) had the following constants: b.p. 184-185°/750 mm; d_4^{20} 1.0175; n_D^{20} 1.5847.; published values, b.p. 184.4°/760 mm; d_4^{20} 1.022; n_D^{20} 1.5863 [13]. Acetanilide, m.p. 113-114°, was prepared for further identification.

(c) N-n-Butylaniline (2.53 g) had the following physical constants: b.p. 95-96°/4.5 mm; d_4^{20} 0.9394; n_D^{20} 1.5393; found MR_D 49.78; calculated MR_D 48.38; EMR_D 1.40. Published values are: b.p. 115-120°/15 mm; d_4^{20} 0.9358; n_D^{20} 1.5381; b.p. 112-114°/9 mm; d_4^{20} 0.9362; n_D^{20} 1.5373 [16].

N-n-Butylbenzanilide was prepared from 2.0 g of the fraction of b.p. 95-96°/4.5 mm and 2.8 g of benzoyl chloride, with 15 ml of 10% caustic soda solution. The crystalline product was dissolved in ether, and the solution was washed successively with water, 5% hydrochloric acid, 5% caustic soda, and water, and dried with anhydrous sodium sulfate. The ether was then distilled off, giving 3.2 g of N-n-butylbenzanilide, which melted at 49-51° after two recrystallizations from n-heptane.

Found %: N 5.58; 5.71

$C_{17}H_{19}ON$. Calculated %: N 5.53

The mixed m.p. with known N-n-butylbenzanilide, m.p. 53-54°, was 49-51.5°. Published m.p. are 55° [17] and 47-48° [18].

(d) 4-Anilinobutan-1-ol (5.70 g) had the following constants: b.p. 147-148°/1.5 mm; d_4^{20} 1.0491; n_D^{20} 1.5638; found MR_D 51.20; calculated MR_D 49.91; EMR_D 1.29.

Found %: N 8.46; 8.66

$C_{10}H_{15}ON$. Calculated %: N 8.48

It was identified as the acid oxalate. A solution of 1.26 g of oxalic acid dihydrate in 7 ml of ethanol was added to 1.65 g of the fraction of b.p. 147-148°/1.5 mm, to give 2.18 g of acid oxalate, which was collected and washed with ethanol. It melted at 124.5-125° (decomposition) after recrystallization from methanol.

Found %: N 5.51; 5.65

$C_{12}H_{17}O_5N$. Calculated %: N 5.49

The m.p. was not changed by mixing with 4-anilinobut-1-yl hydrogen oxalate obtained by reduction of 2-phenyl-3,6-dihydro-ortho-oxazine with zinc dust and acetic acid.

I would like, in conclusion, to express my deep indebtedness to A. N. Nesmeyanov for advising me to study the reaction of diene hydrocarbons with nitrosobenzene, for his unfailing interest in my work, and his valuable advice on its execution.

SUMMARY

1. The reaction between nitrosobenzene and buta-1,3-diene has been studied.

2. Addition takes place according to the diene synthesis, with formation of 2-phenyl-3,6-dihydro-ortho-oxazine.

Received January 2, 1952

Institute of Organic Chemistry,
Academy of Sciences, USSR
M. V. Lomonosov Moscow State University

LITERATURE CITED

[1] R. F. Kleinschmidt, A. C. Cope, J. Am. Chem. Soc. 66, 1929 (1944).

[2] A. C. Cope, L. L. Estes, J. R. Emery, A. C. Haven, J. Am. Chem. Soc. 73, 1199 (1951).

[3] H. Emde, H. Kull, Arch. Pharmaz.Ber. Dtsch.Pharmaz. Ges. 274, 173 (1936);Chem.Cbl. 1, 844 (1937).

[4] D. R. Howton, J. Am. Chem. Soc. 69, 2555 (1947).

[5] R. Baltzly, J.S. Buck, J. Am. Chem. Soc. 65, 1984 (1943); A.M. Mattocks, W. H. Hartung, J. Am. Chem. Soc. 68, 2108 (1946); A. M. Mattocks, W. H. Hartung, J. Biol. Chem. 165, 501 (1946).

[6] O. Wichterle, Collect. Trav. Chim. Tchecosl. 12, 292 (1947).

[7] Yu. A. Arbuzov, Proc. Acad. Sci. USSR, 60, 993 (1948).

[8] O. Wichterle, Collect. Trav. Chim. Tchecosl. 14, 209 (1949).

[9] J. R. Ruhoff, E. E. Reid, J. Am. Chem. Soc. 59, 401 (1937).

[10] C. Paal, G. Otten, Ber. 23, 2587 (1890).

[11] C. A. Bischoff, A. Hausdorfer, Ber. 25, 2270 (1892).

[12] J. W. Bruhl, Ber. 26, 2508 (1893).

[13] Technical Encyclopedia. Handbook of physical, chemical and technological values, Vol. 1, Moscow, 1931.

[14] C. Neuberg, E. Kansky, Biochem. Ztschr. 20, 445 (1909).

[15] R. M. Evans, L. N. Owen, J. Chem. Soc. 239 (1949).

[16] V. C. Sekera, C. S. Marvel, J. Am. Chem. Soc. 55, 345 (1933).

[17] W. H. Mills, J. E. G. Harris, H. Lambourne, J. Chem. Soc. 119, 1294 (1921).

[18] O. Mumm, F. Möller, Ber. 70, 2214 (1937).

BLANK
PAGE

STUDIES OF QUINOLINE DERIVATIVES

PART I. N-ARYL QUATERNARY SALTS OF QUINOLINE DERIVATIVES

G. T. Pilyugin

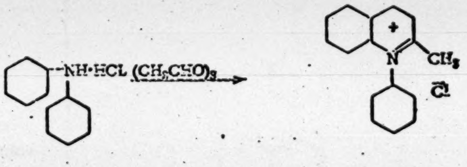
Quaternary salts of heterocyclic based with an alkyl or alkyl-aromatic radical attached to the cyclic nitrogen atom are usually prepared by heating the appropriate bases with alkyl halides, sulfates, or arylsulfonates. N-Aryl salts cannot, however, be prepared by this general method, since aryl halides or arylsulfonates do not give quaternary salts when heated with heterocyclic bases, in view of their low mutual reactivity. This was one of the reasons for the absence from the literature of such quaternary salts and of their derivatives with aryl radicals attached to the cyclic N atom. Herein, too, lies the difficulty of synthesizing N-aryl cyanine dyes of different classes, for which quaternary salts are the basic products.

Kiprianov, Ushenko, and Asnina obtained N-aryl quaternary salts from thiazole derivatives, and used them for the cyanine condensation [1]. Literature references to N-aryl quaternary salts prepared from pyrrole and indolenine derivatives, which are converted into pyrrolo- and indo-cyanines, are to be found [2]. Yet, although heterocyclic compounds containing the quinoline nucleus are among the most commonly encountered of heterocyclic compounds, the N-aryl quaternary salts of quinoline derivatives and their diverse transformations have not been studied at all by organic chemists. For this reason the preparation and study of such salts are of considerable theoretical and practical importance.

We have elaborated a general method for the preparation of N-aryl and N-alkyl quaternary salts of quinoline derivatives. In view of the inapplicability of the usual method, the method depended on the presence of the appropriate aryl or alkyl radical attached to the N atom of the original substance used for synthesis of the heterocycle. These starting substances were secondary arylamines, in which the imino hydrogen is relatively very mobile.

Secondary arylamines and alkarylamines were condensed with paraldehyde or acetaldehyde in acid solution to give N-arylquinoline derivatives (see formulas below).

Thus, for example, the aryl halide salts of quinaldine and its derivatives were obtained from diphenylamine or its derivatives. A study of this reaction showed that it was very convenient to combine cyclization with conversion of the base so obtained into its quaternary salt, both for their subsequent application to the cyanine condensation and for preparation of quinolines and methyleno-derivatives.



The quaternary salts were prepared by heating the secondary arylamines with paraldehyde and hydrochloric or chloric acid in benzene or dioxan solution, in sealed glass tubes at 100°. The quaternary salts obtained were prepared and examined by standard methods. They had definite m.p., and they readily underwent the cyanine condensation, leaving no doubt as to their purity and structure. The arylquinolinium salts obtained are shown in the Table.

Condensation, to give N-aryl quaternary salts, was found to occur in presence of chloric acid, which not only serves as a condensing agent, but also forms the relatively insoluble perchlorate. It was found that attachment

TABLE

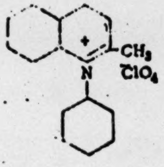
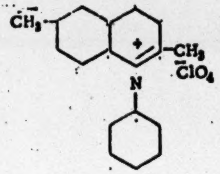
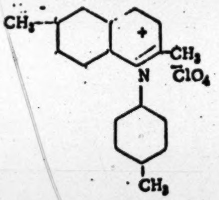
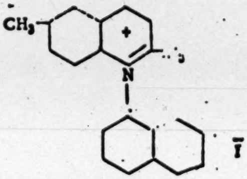
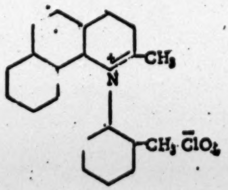
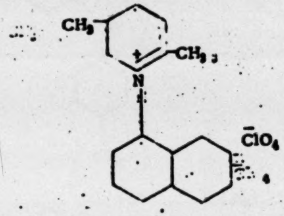
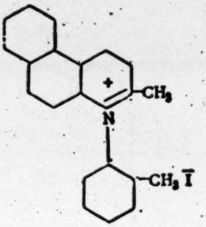
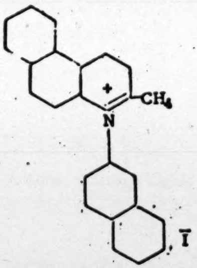
Initial amine	Formula of the quaternary salt obtained	M.p. °C	Yield, %
Diphenylamine		159-160	10.0
4-Methyldiphenylamine		154-155	25.0
4,4'-Dimethyldiphenylamine		193-194	16.0
p-Tolyl-α-naphthylamine		199-200	22.0
o-Tolyl-α-naphthylamine		174-175	15.0

TABLE (Continued)

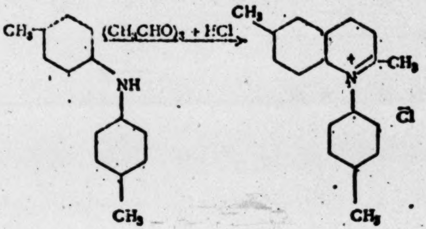
Initial amine	Formula of the quaternary salt obtained	M.p. °C	Yield, %
Phenyl-α-naphthylamine		220	25.0
o-Tolyl-β-naphthylamine		173-174	18.6
β,β'-Dinaphthylamine		200-203	23.0

of an aryl radical to the heterocyclic nitrogen activates an α-methyl group, as was shown by the ease with which cyanine condensation of trinuclear quaternary cyanine salts of halogen acids, but not of sulfonic acids, took place, on the one hand, and by the fact that the quinocyanine condensation proceeds with orthoacetic ester, which is not the case with N-alkyl quaternary salts.

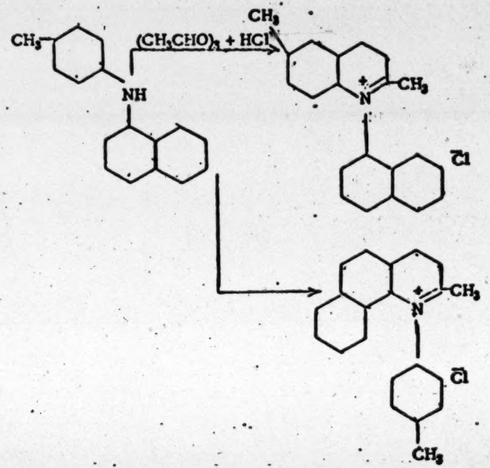
The reactivity of α-methyl groups is thus much greater when an aryl radical is attached to the cyclic nitrogen atom than with an alkyl radical; this difference is due to modified electronic equilibria in that part of the molecule, which also lead to other changes in the properties of the quaternary salts and of the derived dyes. Thus, N-phenyl quaternary salts have lower m.p. and higher solubilities than do the corresponding N-alkyl salts.

The secondary arylamines condensed by us with paraldehyde may yield only a single product, when they have symmetrical molecules (a), or there is an equal probability of forming two products, when the amine is dissymmetrical (b):

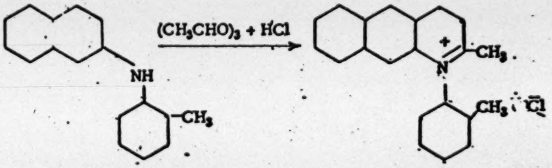
(a)



(b)

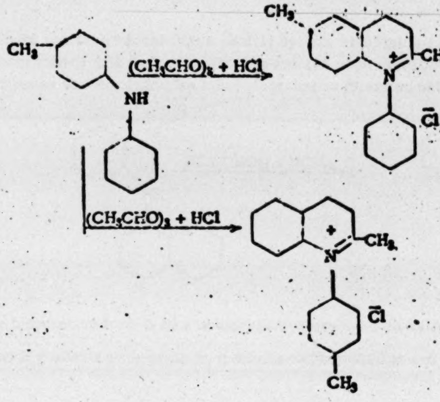


The formation of a third product is possible, although highly improbable, when the dissymmetrical amine contains a β-naphthyl radical



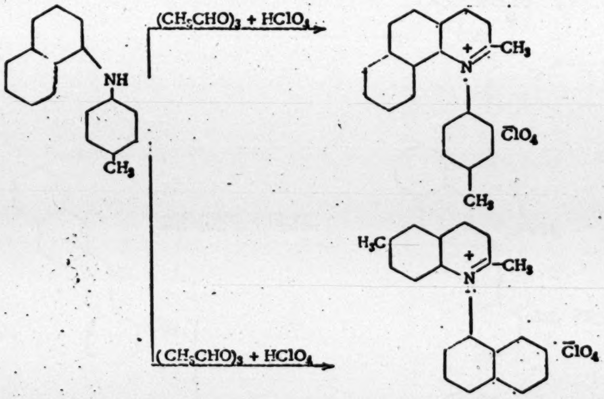
The low probability of this cyclization follows from the preponderance of single bonds between the β,β-atoms of the naphthalene ring, and of double bonds between the α- and β-atoms, as is indicated by numerous known experimental examples. Thus coupling of β-naphthol with diazonium salts takes place exclusively in the α-position, and in the condensation of β-naphthylamine with glycerol the quinoline ring is always closed at the α-atom, and never at the β-carbon atom. In case (b) the quantitative course of the cyclization reaction depends not only on the reactivity of the given radicals, but also on the conditions of cyclization.

Under the fairly uniform conditions in which we conducted the reaction only in two cases did we observe formation of isomeric quaternary salts from dissymmetric amines, to any appreciable extent. Thus 4-methyldiphenylamine may undergo cyclization in the following ways:

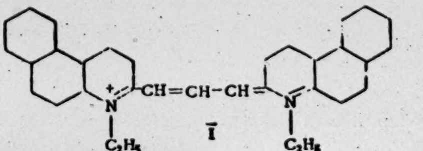


From the theoretical point of view, the probability of formation of quaternary salt of N-phenyl-6-methylquinaldine is the greater one, since the electron donor methyl group substituted in the benzene ring should activate it. We did not, in fact, observe, under our experimental conditions, the less probable case of cyclization with production of N-p-tolylquinaldine. This is confirmed by the fact that the product is a single substance, and by the absorption maximum at 620 mμ of the dye prepared from it. Otherwise the absorption maximum of the dye would tend towards a limiting value of 614 mμ (absorption maximum of a dye with a N-phenyl group); in all probability it would deviate from this value towards the ultraviolet end of the spectrum, as a result of the greater basicity of the p-tolyl than of the phenyl group.

Condensation of p-tolyl-α-naphthylamine may involve two forms of cyclization:

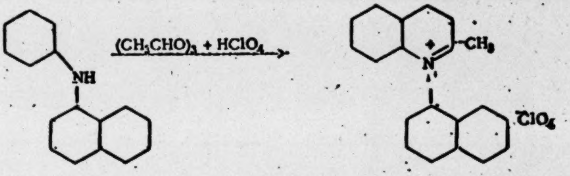


Here, for the same reasons, we may expect that cyclization will take place according to the second variant, with formation of quaternary salt of N-(α-naphthyl)-6-methylquinaldine. The product is a single substance, yielding a carbocyanine with an absorption maximum at 625 mμ, whereas with cyclization in the other direction the absorption maximum of the derived dye would exceed that of the known carbocyanine



I

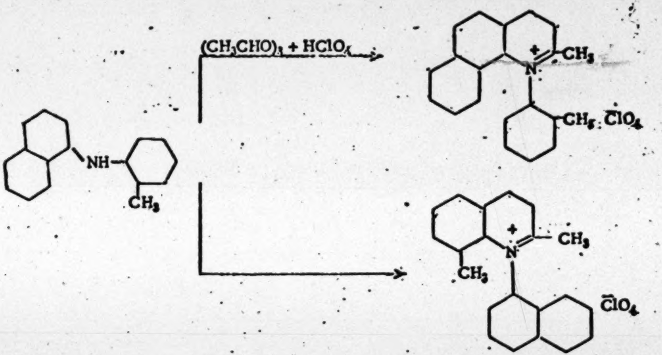
of 634 mμ [3]. There can be no doubt that a similar dye not containing a N-p-tolyl group would have an absorption maximum shifted still further towards the red end of the spectrum, which is not in fact the case. We similarly established that condensation takes place in one direction only with phenyl-α-naphthylamine


NH
(CH₃CHO)₃ + HClO₄
CH₃
N
ClO₄

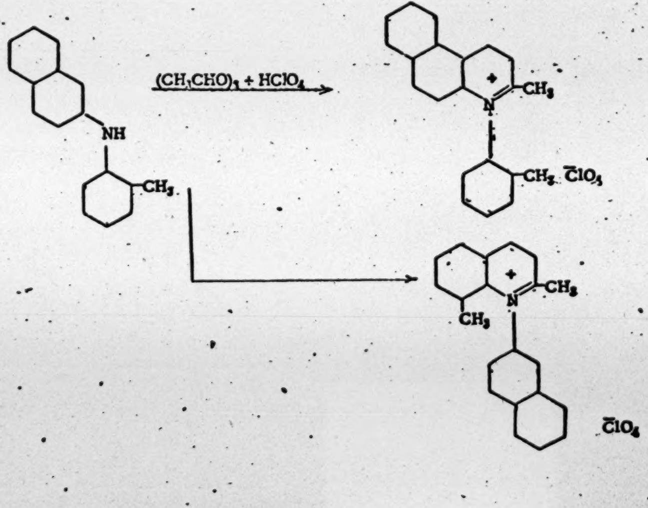
as is shown by the preparation from it of a quinocarbocyanine with an absorption maximum at 618 mμ.

Two isomeric products were given by o-tolyl-α-naphthylamine and by o-tolyl-β-naphthylamine:

(a)


(CH₃CHO)₃ + HClO₄
NH
CH₃
N
CH₃
CH₃ ClO₄
CH₃
CH₃
ClO₄

(b)


NH
CH₃
(CH₃CHO)₃ + HClO₄
N
CH₃
CH₃ ClO₄
CH₃
CH₃
ClO₄

The main reaction products were quaternary salts with N-o-tolyl groups. The green carbocyanines prepared therefrom had the following optical properties:

(a) bis-[N-o-tolyl-7,8-benzoquinoline-(2)]-trimethinecyanine perchlorate – absorption maximum in ethanol 642 mμ.

(b) bis-[N-o-tolyl-5,6-benzoquinoline-(2)]-trimethinecyanine perchlorate – absorption maximum 644 mμ.

The isomeric quaternary salts with N-α-or N-β-naphthyl radicals were obtained in small yields only. They gave positive reactions for formation of blue quinocarbocyanines, which are being studied by us. Thus the quaternary salts with N-aryl groups, derivatives of quinaldine, have so far been introduced into the cyanine condensation only, for the purpose of preparing sensitizing dyes.

EXPERIMENTAL

N-Phenylquinaldine perchlorate. 4 g of diphenylamine hydrochloride was heated at 80-110° with 2 g of paraldehyde in dioxan, in a sealed tube. The semi-solid, tacky product was washed with ether, and was taken without further purification for cyanine condensation with orthoformic acid, which proceeded smoothly. This condensation product was extracted repeatedly with boiling ethanol, and the extract was evaporated to dryness, leaving a dark-colored, sticky residue, which was washed 2-3 times with ether, and dissolved in a small volume of ethanol. The quaternary salt was precipitated from this solution by adding a saturated solution of potassium perchlorate. The light brown precipitate was filtered off, and the filtrate was evaporated on the water bath until drops of oil formed, when it was cooled and filtered; the quaternary salt collected was recrystallized from water. N-Phenyl-quinaldine crystallizes in needles, m.p. 159-160°, of a faint yellow color. It is readily soluble in ethanol and in hot water, and is sparingly soluble in cold water. The yield is 10% of theoretical.

Found %: Cl 11.32
$C_{16}H_{14}NClO_4$. Calculated %: Cl 11.60

N-Phenyl-6-methylquinaldine perchlorate. 3.3 g of 4-methyldiphenylamine, 2.5 ml of benzene, 1.5 ml of 35% chloric acid, and 1.8 ml of paraldehyde were heated in a sealed tube for 10 hrs at 100°, giving a thick, dark red liquid. The product was washed with a few portions of ether, and was dissolved in a small volume of ethanol, from which it crystallized out. Recrystallization from ethanol gave 1.35 g (25% of theoretical) of light orange, finely crystalline product, m.p. 154-155°.

Found %: Cl 10.40
$C_{17}H_{16}NClO_4$. Calculated %: Cl 10.66

N-(p-tolyl)-6-methylquinaldine perchlorate. 2 g of 4,4'-dimethyl-diphenylamine, 2 ml of benzene, 2 ml of 35% chloric acid, and 1.4 ml of paraldehyde (added at 0°) were heated at 100° for 15 hrs in a sealed tube; the use of more concentrated chloric acid led to formation of tarry products. Shortening the reaction time lowers the yield of quaternary salt, whereas prolonging it leads to deterioration in the quality of the salt, and renders its purification difficult. The reaction product, which was a viscous, dark red liquid, was washed with small portions of ether, until the ether ceased to be colored, and the residue was dissolved in a small volume of ethanol, from which the salt crystallized. The salt was washed with alcohol and ether, and recrystallized from ethanol, giving 0.55 g (16% of theoretical) of colorless finely crystalline salt, m.p. 193-194°.

Found %: Cl 10.22
$C_{18}H_{15}NClO_4$. Calculated %: Cl 10.33

N-(α-naphthyl)-6-methylquinaldine iodide. 2 g p-tolyl-(α-naphthyl)-amine, 2 ml of benzene, 1 ml of hydrochloric acid, and 1.5 ml of paraldehyde were heated in a sealed tube for 10 hrs at 100° giving a dark red viscous oil, which solidified after extraction with ether. The product was repeatedly extracted with boiling ethanol, until the extract became colorless. The hot extract was filtered and evaporated down to small volume, when 4 ml of saturated potassium iodide solution was added, the solution was boiled, and filtered hot. The filtrate was evaporated until an oily surface film appeared, when it was left overnight and filtered in the morning. The yellow crystalline product (yield 22% of theory) melts at 199-200° (decomposition).

Found %: I 30.48
$C_{21}H_{18}NI$. Calculated %: I 30.83

N-(o-tolyl)-7,8-benzoquinaldine perchlorate. A mixture of 3.8 g of o-tolyl-α-naphthylamine, 2.2 g of paraldehyde, 1.5 ml of hydrochloric acid (d 1.19) and 4 ml of benzene in a sealed tube was cooled strongly, shaken vigorously, and heated in a boiling water bath for 8 hrs. The product was a gelatinous, bordeaux-colored mass, which was extracted with ether until the extracts became colorless; the residue was then a yellow powder. This powder was extracted repeatedly with boiling ethanol, the extract was evaporated down to small volume, and saturated aqueous potassium perchlorate was added, to give a salt which melted at 173-174°, after recrystallization from aqueous ethanol; yield 15% of theoretical.

Found %: Cl 9.16
$C_{21}H_{18}NClO_4$. Calculated %: Cl 9.37

N-α-naphthylquinaldine perchlorate. 2 g of N-α-naphthylaniline, 1.3 ml of paraldehyde, 0.5 ml of 38% chloric acid, and 2 ml of benzene were heated at 100° for 10 hrs, in a sealed tube. The dark red product was extracted with ether, when it became solid, and was recrystallized from ethanol, giving a finely crystalline powder, which was collected, washed with ether, and recrystallized from aqueous ethanol, giving 1.8 g (25% of theoretical) of salt, m.p. 220° (decomposition).

Found %: Cl 9.44
$C_{20}H_{16}NClO_4$. Calculated %: Cl 9.60

N-(o-tolyl)-5,6-benzoquinaldine iodide. A mixture of 3.4 g of o-tolyl-β-naphthylamine, 1.9 g of paraldehyde, 1.4 g of hydrochloric acid (d 1.19), and 2 ml of benzene was heated at 100° for 16 hrs, in a sealed tube. The solid product was repeatedly extracted with ether, and then dissolved in 10 ml of boiling ethanol. Saturated aqueous potassium iodide was added to the solution, from which the quaternary salt separated on cooling. It was collected, washed with ether, dried, and recrystallized from aqueous ethanol, giving 1.1 g (18.6% of theoretical) of a yellowish, finely crystalline product, m.p. 173°.

Found %: I 31.40
$C_{21}H_{18}NI$. Calculated %: I 31.95

N-β-naphthyl-5,6-benzoquinaldine iodide. A mixture of 3 g of β,β'-dinaphthylamine, 1.6 g of paraldehyde, 1 ml of hydrochloric acid (d 1.19), and 3 ml of benzene was heated at 100° for 8 hrs, in a sealed tube. The dark red, viscous, oily product was repeatedly extracted with ether, until the extracts became colorless. The bordeaux-colored, semi-solid residue, which consists chiefly of quaternary salt is extracted 2-3 times with small portions of hot ethanol, and 4 ml of saturated aqueous potassium iodide was added to the dark red extract, giving a light brown precipitate of quaternary salt, which is collected, washed with ether, and dried at 110°; yield of crude salt 70% of theory. The salt gave the cyanine condensation reaction. Recrystallization from aqueous ethanol gave 1.6 g (32% of theory) of pale yellow crystalline salt, m.p. 200-203°.

Found %: I 28.10
$C_{24}H_{18}NI$. Calculated %: I 28.35

SUMMARY

1. Condensation of secondary arylamines with paraldehyde gives a series of N-aryl substituted quinolines.

2. Eight quaternary N-arylquinolinium salts have been prepared and described, in which the N-aryl radical is phenyl, o-tolyl, p-tolyl, α-naphthyl, and β-naphthyl.

Received June 23, 1951

Academy of Sciences USSR
Institute of Organic Chemistry
Chernovitsy State University

LITERATURE CITED

[1] A. I. Kiprianov, F. I. Asnina, and I. K. Ushenko. J. Gen. Chem. 18, 165 (1948); A. I. Kiprianov and I. K. Ushenko. J. Gen. Chem. 17, 2201 (1947).

[2] L. G. S. Brooker, J. Am. Chem. Soc. 67, 1869 (1945).

[3] F. Hamer, Beilenson, Proc. Roy. Soc. 1437 (1937); L. G. S. Brooker, F. L. White, R. H. Spraque, J. Am. Chem. Soc. 73, 1087 (1951).

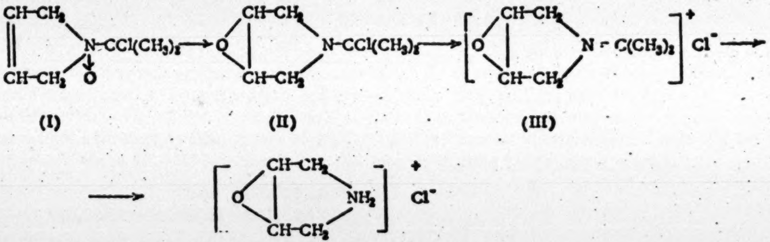
REACTIONS OF DIENE HYDROCARBONS WITH NITROSO-COMPOUNDS

REACTION OF BUTA-1,3-DIENE, 2,3-DIMETHYLBUTA-1,3-DIENE, AND CYCLOHEXA-1,3-DIENE WITH 1-CHLORO-1-NITROSOCYCLOHEXANE

Yu. A. Arbuzov and A. Markovskaya

Wichterle [1] found in 1947 that buta-1,3-diene reacts with 2-chloro-2-nitrosopropane in benzene, in presence of ethanol, to give a crystalline product, C_4H_8ONCl, m.p. 153°. The product obtained in absence of ethanol is a tarry substance, insoluble in benzene, which was converted into the above substance, m.p. 153°, by treatment with a small amount of water or ethanol. The same product is obtained from buta-1,3-diene and 1-chloro-1-nitrosocyclohexane in benzene and ethanol as with 2-chloro-2-nitrosopropane. By the action of alkali on an aqueous solution of the substance of m.p. 153° Wichterle obtained a liquid product, b.p. 50-52°/20 mm, which he supposed to be 3,4-oxidopyrrolidine, of which the substance of m.p. 153° was the hydrochloride.

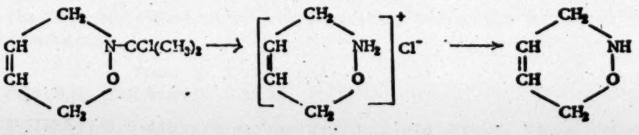
Wichterle explained the formation of this hydrochloride in the following way. The first product of the reaction between butadiene and 2-chloro-2-nitrosopropane is the N-oxide (I), which undergoes transformation into a 3,4-oxidopyrrolidine derivative (II), which is a chloride of the pseudo-base. Compound (II) undergoes further rearrangement to the quaternary salt (III), which then undergoes hydrolysis or alcoholysis to give 3,4-oxidopyrrolidine hydrochloride (IV):


(I) (II) (III)

(IV)

It has been shown [2-5] that diene hydrocarbons react with aromatic nitroso-compounds according to the diene synthesis, with formation of 3,6-dihydro-ortho-oxazine derivatives.

It was reasonable to suppose that the reaction of buta-1,3-diene with chloronitroso-compounds should also proceed according to the diene synthesis with formation of the N-derivative of 3,6-dihydro-ortho-oxazine (V), which then undergoes hydrolysis (or alcoholysis), with formation of 3,6-dihydro-ortho-oxazine hydrochloride (VI). Wichterle's base, b.p. 50-52°/20 mm, should thus have the structure of 3,6-dihydro-ortho-oxazine (VII).

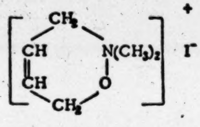

(V) (VI) (VII)

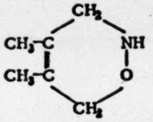
Confirmation of the correctness of structure (VII) for the base C_4H_7ON was provided in 1949 by Finkelshtein, Arbuzov, and Shorygin [6], who showed that the Raman spectrum of this base (b.p. 50.5°/19 mm; d_4^{20}

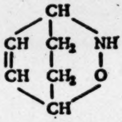
1.0714; n_D^{20} 1.4893) contained a frequency corresponding to a C=C bond, with an intensity characteristic of an isolated C=C bond. In 1950 Wichterle and Novak [7] published a paper in which they admitted the correctness of Yu. A. Arbuzov's 3,6-dihydro-ortho-oxazine structure (VII) for the base C_4H_7ON.

The present paper describes the results of a study of the reactions between buta-1,3-diene, 2,3-dimethylbuta-1,3-diene, and cyclohexa-1,3-diene with 1-chloro-1-nitrosocyclohexane in ethereal solution, in presence of ethanol. Buta-1,3-diene and 1-chloro-1-nitrosocyclohexane gave 3,6-dihydro-ortho-oxazine hydrochloride (VI), from which 3,6-dihydro-ortho-oxazine (VII) was obtained; a number of its derivatives was prepared for its identification, such as the methiodide of 2-methyl-3,6-dihydro-ortho-oxazine (VIII), from methyl iodide and 3,6-dihydro-ortho-oxazine (VII), and the 3,5-dinitrobenzoyl and 2,4-dinitrophenyl derivatives and the picrate, by standard methods.

1-Chloro-1-nitrosocyclohexane and 2,3-dimethylbuta-1,3-diene give 4,5-dimethyl-3,6-dihydro-ortho-oxazine hydrochloride, from which the free base (IX) is prepared; its picrate and 3,5-dinitrobenzoate are described.


(VIII)


(IX)


(X)

1-Chloro-1-nitrosocyclohexane and cyclohexa-1,3-diene afford 3,6-endoethyleno-3,6-dihydro-ortho-oxazine hydrochloride, from which the free base (X), a colorless, waxy substance, was obtained, as well as its crystalline picrate and benzoyl and 3,5-dinitrobenzoyl derivatives.

EXPERIMENTAL

3,6-Dihydro-ortho-oxazine hydrochloride. 62 g of buta-1,3-diene was added to a solution of 59.0 g (0.4 mol) of 1-chloro-1-nitrosocyclohexane in 150 ml of ether and 58 ml of ethanol, at 0°. Colorless needle-shaped crystals began to separate within 30 minutes. The flask was left for 3 days at 0°, during which time the color of the solution changed from blue-violet to light brown. The crystalline deposit was collected and washed with absolute ether, giving 35.2 g (72.4% of theoretical) of hydrochloride, m.p. 149-151° (decomposition), rising to 151-152° (decomposition) after recrystallization from absolute ethanol.

Found %: Cl 29.11; 29.24
C_4H_8ONCl. Calculated %: Cl 29.17

3,6-Dihydro-ortho-oxazine. 45 g of caustic potash was added gradually, cooling at 0°, to a solution of 48.6 g (0.4 mol) of 3,6-dihydro-ortho-oxazine hydrochloride in 40 ml of water, the potassium chloride forming was filtered off, and the filtrate was thrice extracted with ether. The combined ethereal extracts were dried with fused potassium hydroxide, and the ether was distilled off, giving 30.9 g (90.9%) of 3,6-dihydro-ortho-oxazine, a colorless mobile liquid having the following constants: b.p. 50.5-51°/19 mm; d_4^{20} 1.0702; n_D^{20} 1.4891; found MR_D 22.95; calculated MR_D 23.23.

Found %:	C 56.37; 56.28;	H 8.27; 8.29;	N 16.30; 16.31
C_4H_7ON. Calculated %:	C 56.45;	H 8.29;	N 16.46

The picrate of 3,6-dihydro-ortho-oxazine crystallizes from water as long yellow needles, m.p. 163-164° (decomposition).

Found %: N 17.77; 17.57
$C_{10}H_{10}O_8N_4$. Calculated %: N 17.83

2-Methyl-3,6-dihydro-ortho-oxazine methiodide. 5 ml of methanol, 1.7 g of sodium bicarbonate, and 5 ml of methyl iodide were added to 1.22 g (0.01 mol) of 3,6-dihydro-ortho-oxazine hydrochloride, and the mixture was boiled under reflux for $2\frac{1}{2}$ hrs., and was filtered hot. Platelets of 2-methyl-3,6-dihydro-ortho-oxazine methiodide, m.p. 132.5-133° (decomposition) after recrystallization from methanol, separated from the filtrate on cooling, in 83% yield (2.0 g). The m.p. given by Wichterle and Novak [7] is 133° (decomposition).

Found %: I 52.87; 52.91
$C_6H_{12}ONI$. Calculated %: I 52.65

2-(3',5'-dinitrobenzoyl)-3,6-dihydro-ortho-oxazine. A mixture of 0.61 g (0.005 mol) of 3,6-dihydro-ortho-oxazine hydrochloride, 1.15 g (0.005 mol) of 3,5-dinitrobenzoyl chloride, and 2 ml of dry pyridine was heated at 100° for 10 min., cooled, and treated with 3 N hydrochloric acid. The precipitate was collected, washed with 5% hydrochloric acid, 2% aqueous sodium carbonate, and water, successively, and recrystallized from methanol, giving 0.61 g (43.6%) of faint yellow crystals, m.p. 142.5°.

Found %: C 47.38; 47.42; H 3.40; 3.34; N 14.92; 14.96
$C_{11}H_9O_6N_3$. Calculated %: C 47.32; H 3.25; N 15.05

2-(2',4'-dinitrophenyl)-3,6-dihydro-ortho-oxazine. A mixture of 0.43 g (0.005 mol) of 3,6-dihydro-ortho-oxazine, 1.01 g (0.005 mol) of chloro-2,4-dinitrobenzene, 0.6 g of anhydrous potassium acetate, and 10 ml of absolute alcohol were heated at 100° under reflux for 2 hrs and 20 ml of water was added to the cooled mixture. The precipitate was collected, washed with water, and recrystallized from acetone, giving 0.66 g (52.4%) of large yellow crystals, m.p. 142.5° (decomposition).

Found %: N 16.42; 16.39
$C_{10}H_9O_5N_3$. Calculated %: N 16.73

4,5-Dimethyl-3,6-dihydro-ortho-oxazine hydrochloride. 22.2 g (0.27 mol) of 2,3-dimethylbuta-1,3-diene was added to a solution of 36.9 g (0.25 mol) of 1-chloro-1-nitrosocyclohexane in 90 ml of ether and 33 ml of ethanol at 0°, and the mixture was kept at 0° for 12 hrs and at room temperature for 3 days, during which time its color changed from blue-violet to green. The crystalline deposit was collected and washed with ether; yield 13.0 (34.8%), m.p. 149-150° (decomposition), after recrystallization from absolute alcohol.

Found %: C 48.00; 47.90; H 8.16; 8.29; N 9.27; 9.22; Cl 24.21; 24.32
$C_6H_{12}ONCl$. Calculated %: C 48.16; H 8.09; N 9.36; Cl 23.70

4,5-Dimethyl-3,6-dihydro-ortho-oxazine. 11.2 g of caustic potash was added gradually, with cooling, to a solution of 15.0 g (0.1 mol) of 4,5-dimethyl-3,6-dihydro-ortho-oxazine hydrochloride in 10 ml of water at 0°, the potassium chloride forming was filtered off, the filtrate was extracted with ether, and the ether extract was dried with anhydrous sodium sulfate. It contained 8.1 g (71.7% yield) of 4,5-dimethyl-3,6-dihydro-ortho-oxazine, a colorless mobile liquid, b.p. 83.5-84°/20 mm; d_4^{20} 1.0027; n_D^{20} 1.4863; found MR_D 32.42; calculated MR_D 32.46.

Found %: C 63.27; 63.26; H 9.88; 9.82; N 12.57; 12.51
$C_6H_{11}ON$. Calculated %: C 63.68; H 9.80; N 12.38;

The picrate of 4,5-dimethyl-3,6-dihydro-ortho-oxazine melted at 169-170° (decomposition), after recrystallization from water.

Found %: N 16.30; 16.34. $C_{12}H_{14}O_8N_4$. Calculated %: N 16.37.

2-(3',5'-dinitrobenzoyl)-4,5-dimethyl-3,6-dihydro-ortho-oxazine. A mixture of 0.58 g (0.0025 mol) of 3,5-dinitrobenzoyl chloride, 0.37 g (0.0025 mol) of 4,5-dimethyl-3,6-dihydro-ortho-oxazine hydrochloride, and 1 ml of dry pyridine gave 0.5 g (64.9%) of this product, m.p. 168.5°, after recrystallization from methanol.

Found %: C 50.86; 50.70; H 4.43; 4.35; N 13.61; 13.68
$C_{13}H_{13}O_6N_3$. Calculated %: C 50.81; H 4.26; N 13.68

3,6-endoethyleno-3,6-dihydro-ortho-oxazine hydrochloride. 4.0 g (0.05 mol) of cyclohexa-1,3-diene is added, cooling in ice, to a solution of 6.64 g (0.045 mol) of 1-chloro-1-nitroso-cyclohexane in 16 ml of ether and 6 ml of ethanol. The mixture was left on ice for 30 min, by which time a considerable amount of crystalline product had formed, and it was then kept at room temperature for 6 hrs, and filtered. The crystalline product was recrystallized from ethanol, giving 5.91 g (89.0%) of the salt, m.p. 147-147.5° (decomposition).

Found %: C 48.85; 48.65; H 7.01; 7.17; N 9.59; 9.56; Cl 23.97; 23.75
$C_6H_{10}ONCl$. Calculated %: C 48.82; H 6.83; N 9.49; Cl 24.02

3,6-endoethyleno-3,6-dihydro-ortho-oxazine. 5.4 g of caustic potash was added gradually, with cooling, to a solution of 10.0 g (0.068 mol) of 3,6-endoethyleno-3,6-dihydro-ortho-oxazine hydrochloride in 6 ml of water, the precipitate of potassium chloride was filtered off, and the filtrate was extracted three times with ether, the ethereal extract was dried with anhydrous sodium sulfate, and the ether was distilled off in vacuum, leaving a white waxy residue. This was recrystallized from cyclohexane, giving 6.60 g (87.7%) of white, waxy product, m.p. ~72°.

Found %: C 64.56; 64.62; H 8.21; 8.52
C_6H_9ON. Calculated %: C 64.84; H 8.16

The picrate of 3,6-endoethyleno-3,6-dihydro-ortho-oxazine melted at 147.5-148° (decomposition), after recrystallization from water.

Found %: N 16.59; 16.62
$C_{12}H_{12}O_8N_4$. Calculated %: N 16.47

2-Benzoyl-3,6-endoethyleno-3,6-dihydro-ortho-oxazine. 2.1 g (0.01 mol) of benzoyl chloride was added in three portions, with violent shaking, to a mixture of 1.11 g (0.01 mol) of 3,6-endoethyleno-3,6-dihydro-ortho-oxazine in 10 ml of 10% aqueous caustic soda, the precipitate was dissolved in ether, the extract was washed successively with water, 5% aqueous caustic soda, 3% hydrochloric acid, and water, the ether was distilled off, and the residue was recrystallized from ethanol, giving 1.55 g (72.1%) of product, m.p. 109°.

Found %: C 72.27; 72.34; H 6.32; 6.44; N 6.61; 6.77
$C_{13}H_{13}O_2N$. Calculated %: C 72.54; H 5.09; N 6.51

2-(3',5'-dinitrobenzoyl)-3,6-endoethyleno-3,6-dihydro-ortho-oxazine. 0.37 g (0.0025 mol) of 3,6-endoethyleno-3,6-dihydro-ortho-oxazine hydrochloride, 0.58 g (0.0025 mol), of 3,5-dinitrobenzoyl chloride, and 1 ml of dry pyridine, gave a product melting at 166.5-167° (decomposition), after recrystallization from methanol; yield 0.64 g (84.2%).

Found %: C 51.15; 51.12; H 3.81; 3.87; N 13.95; 14.10
$C_{13}H_{11}O_6N_3$. Calculated %: C 51.15; H 3.63; N 13.77

Received October 15, 1951

Institute of Organic Chemistry
Academy of Sciences USSR
M. V. Lomonosov State University

LITERATURE CITED

[1] O. Wichterle, Collect. Trav. Chim. Tchecosl. 12, 292 (1947).

[2] Yu. A. Arbuzov, Proc. Acad. Sci. USSR, 60, 993 (1948).

[3] Yu. A. Arbuzov and N. I. Fedyukina. Proc. Acad. Sci. USSR, 60, 1173 (1948).

[4] Yu. A. Arbuzov and T. A. Mastryukova. Sci. Memoirs Moscow State Univ. 132, 174 (1950).

[5] Yu. A. Arbuzov, N. L. Fedyukina, V. V. Shavyrina, and R. I. Shepeleva. Sci. Memoirs Moscow State Univ. 132, 190 (1950).

[6] A. I. Finkelshtein, Yu. A. Arbuzov, and P. P. Shorygin, J. Phys. Chem. 24, 802 (1950).

[7] O. Wichterle, J. Novak, Collect. Trav. Chim. Tchecosl. 15, 309 (1950).

DISCUSSION

DISTRIBUTION OF π-ELECTRON DENSITY AND INTERATOMIC DISTANCES. 2

G. V. Bykov

In my first paper on this subject [1] the basic principles of the hypothesis of π-electron distribution were presented, equations were derived for the calculation of interatomic distances and π-electron charges of bonds, and, on the example of CC and CH bonds in unsaturated and aromatic hydrocarbons, the advantages of the proposed method over other ones explaining experimental data relating to interatomic distances in these compounds, were pointed out. The present paper, which is a direct continuation of the former one, extends the π-electron distribution hypothesis to the most important of the remain-types of bonds occurring in organic compounds.

CCl, CBr, and CI bonds. The length of the σ-bond between carbon and halogen in compounds of the types CX_4 and CH_3X varies, as is known. The second type is, of course, more characteristic of organic halogen compounds. For this reason we take as standard lengths of CX bonds those determined spectroscopically in methyl chloride, iodide, and bromide, viz., $L_{CCl} = 1.779$, $L_{CBr} = 1.936$ and $L_{CI} = 2.132$. The lengths of the bonds in the corresponding dihalogenoethylenes are $l_{CCl} = 1.640$ and $l_{CC} = 1.195$; $l_{CBr} = 1.80 \pm 0.03$ and $l_{CC} = 1.20 \pm 0.03$; $l_{CI} = 2.03 \pm 0.10$ and $l_{CC} = 1.18$. The calculation of specific striction from these figures seems scarcely possible for CBr and CI bonds, although the calculated value of Δ_{CBr} is indirectly confirmed (v.i.).

For the calculation of Δ_{CX} we use formula (6), whence $\Delta_{CX} = \dfrac{L_{CX} - l_{CX}}{A_{CX}}$; according to formula (11) $2A_{CX} + A_{CC} = 4$, and hence

$$\Delta_{CX} = \frac{L_{CX} - l_{CX}}{2 - \dfrac{L_{CC} - l_{CC}}{2\Delta_{CC}}}$$

Calculating from this formula we obtain:

$$\Delta_{CCl} = 0.166;\ \Delta_{CBr} = 0.16 \text{ and } \Delta_{CI} = 0.13.$$

We shall now consider certain experimental data.

The CCl bond approaches the value of the ethylenic bond in vinyl chloride ($l_{CCl} = 1.69 \pm 0.02$); isocrotyl chloride (1.72 ± 0.02); 1,2-dichloroethylene (1.69 ± 0.02, or what seems to be too low a value, 1.67 ± 0.03); 1,1-dichloroethylene (1.69 ± 0.02); trichloroethylene (1.72 ± 0.02); tetrachloroethylene (1.73 ± 0.02; 1.71 ± 0.02). The magnitude of the π-electron charge calculated from equation (8) fluctuates within the limits $A_{CCl} = 0.5 \pm 0.1\,\pi$ (in vinyl chloride and dichloroethylenes) to $A_{CCl} = 0.3 \pm 0.1\,\pi$ (in tetrachloroethylene), i.e., it is in all cases greater than $A_{CH} = 0.14\,\pi$ in ethylene. The same picture is given by the chlorinated benzenes: hexachlorobenzene (1.70 ± 0.03); 1,2,4,5-tetrachlorobenzene (1.72 ± 0.04); 1,3,5-trichlorobenzene (1.69 ± 0.03); m- and p-dichlorobenzene (1.69 ± 0.03); o-dichlorobenzene (1.71 ± 0.03), and chlorobenzene (1.69 ± 0.03).

The length of the CBr bond approaches that of the ethylenic bond, in vinyl bromide (1.86 ± 0.04); dibromoethylene (1.85 ± 0.04; 1.91 ± 0.05 and 1.86 ± 0.04); and tetrabromoethylene (1.91 ± 0.05), and in aromatic compounds: 1,3,5-tribromobenzene (1.84 ± 0.02); p-dibromobenzene (1.88 ± 0.02); o-dibromobenzene (1.89); 4,5-dibromo-o-xylene (1.88 ± 0.02); 5,6-dibromodihydroindene (1.84 ± 0.02); 6,7-dibromotetralin (1.86 ± 0.02); 3,3'-dibromodiphenyl (1.88). The value of the π-electron charge of the CBr bonds varies from $A_{CBr} = 0.6\,\pi$ to $A_{CBr} = 0.2\,\pi$.

There are very few available figures for the CI bond, and since the determination of Δ_{CI} itself is insufficiently accurate we do not propose to analyze these figures, but shall confine ourselves to remarking that in general they are not in conflict with the assumptions that will be made further on in this paper.

The reason why the value of A_{CX} in halogen derivatives of ethylene and benzene is greater than that of A_{CH} in ethylene and benzene may in all probability be sought, within the limits of the π-electron distribution hypothesis, in the passage of π-electron charges of CC and CH bonds to CX bonds. As a result, in the series $C_2H_3X - C_2H_2X_2 - C_2HX_3 - C_2X_4$, the π-electron charges of CX bonds (and also of CC bonds) should diminish, and their length should increase. In general, as appears from the above-cited data, these consequences are confirmed by experiment, insofar as concerns the CX bond (sufficiently accurate data are not available for CC bonds). As applied to aromatic halogen derivatives, it follows from these conclusions that the π-electron charge of CCl bonds in the ortho-position (or generally in the vicinal position) will be smaller, and the length of the bond will be greater, than in the para- or the meta-position. The data available for chloro-derivatives are not in conflict with this conclusion.*

CO bond. In view of the lack of data for CO σ-bonds, accurate to the third decimal,** we are obliged to take the arithmetic mean of the values for the length of CO bonds in methyl ether (1.42 ± 0.03); ethanol (1.43 ± 0.02); ethylene glycol (1.43; 1.43 ± 0.02); trioxymethylene (1.42 ± 0.03; 1.40 ± 0.02); pentaerythritol (1.46 ± 0.03); paraldehyde (1.43 ± 0.02); methanol (1.44 ± 0.01); ethylene chlorohydrin (1.43); dioxyethylenemethylene (1.42 ± 0.03); methylal (1.42 ± 0.02); glycerol (1.43); tetrahydrofuran (1.43 ± 0.03); dioxan (1.46 ± 0.04, 1.42; 1.44 ± 0.03); and ethyl ether (1.43 ± 0.02). $L_{CO} = 1.43$.

Data for the length of the bond in carbon monoxide, $l_{CO} = 1.129$, in carbon dioxide, $l_{CO_2} = 1.159$, or, according to other estimates, $l_{CO} = 1.1632$, can be applied to the determination of the specific striction of the CO bond. An argument against the use of data relating to carbon dioxide is that it contains cumulated double bonds, similarly to allene, and, as will be shown later, $\Sigma S < n$ for such compounds. On the other hand, carbon monoxide is generally considered as an anomalous compound, and some authors believe that its molecule may, similarly to that of nitrogen, develop a triple bond. The closeness of the lengths of the bonds in carbon monoxide and dioxide suggests that this is a very doubtful assumption, and that, until more convincing basic data are forthcoming, carbon monoxide may be accepted as a substance with a "normal" double bond, for the purpose of calculating Δ_{CO}:

$$\Delta_{CO} = \frac{L_{CO} - l_{CO}}{A_{CO}} = \frac{1.43 - 1.13}{2} = 0.15.$$

We shall now consider certain facts relating to interatomic distances in oxygen-containing organic compounds. The length of the CO bond in ketones and aldehydes varies within narrow limits: formaldehyde (1.21 ± 0.01; 1.225); glyoxal (1.20 ± 0.01); acetaldehyde (1.22 ± 0.02); diacetyl (1.20 ± 0.02); the values for CO bonds of carboxylic acids and esters are close to these: oxalic acid (1.22; 1.20); formic acid (1.225 ± 0.02); acetic acid (1.24 ± 0.03); methyl formate (1.21 ± 0.03); methyl acetate (1.22 ± 0.03), arithmetic mean $l_{CO} = 1.22 \pm 0.02$. According to formula (8) $A_{CO} = 1.4 \pm 0.1\ \pi$. The π-electron charge $A' = 2 - A_{CO} = 0.6 \pm 0.1\ \pi$ is shared between two CC bonds (in ketones), and between CC and CH bonds (in aldehydes), between CH and CO bonds (in formic acid or its esters), and between CC and CO bonds (in other carboxylic acids and their esters). As may, however, be concluded from interatomic distances, competition between CO and CH or CC bonds leads to practically the whole of the charge A' being transferred to the CO bond. The length of the simple CO bond in these compounds, as calculated from formula (7), should then have the limiting value $l_{CO} = 1.34$. In fact, the length of the CO hydroxyl bond of formic acid is (1.368 ± 0.03); of methyl formate (1.36 ± 0.04); and of methyl acetate (1.36 ± 0.04). This obliges us to regard the determinations of the length of the CO hydroxyl bond in acetic acid ($l_{CO} = 1.43 \pm 0.03$) with some doubt.

Transfer of most of the π-electron charge A' to the CO bond is also observed when this bond is vicinal to an ethylenic, instead of a carbonyl bond. Thus in vinyl ether $l_{CO} = 1.40 \pm 0.03$ and $l_{CC} = 1.34 \pm 0.03$; in furan $l_{CO} = 1.40 \pm 0.02$; and in dioxadiene $l_{CO} = 1.41 \pm 0.03$; and since $2A_{CH} = 0.28\ \pi$ for ethylene [1], it follows from formula (7) that $l_{CO} = 1.43 - 0.28 - 0.15 = 1.39$, for the limiting case of transfer of the whole of the π-electron charge from the CH to the CO bond.

---

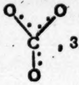
* Only in hexachlorobenzene is the greatest length of the CCl bond to be expected. The determination of the length of the CC bonds of this compound would be of particular interest; it should exceed that of CC bonds of other halogen derivatives of benzene.

** It is true that the length of the CO bond of ethylene oxide, as determined spectroscopically, is $l_{CO} = 1.4363$, but the length of the CC bond of this compound, $l_{CC} = 1.4728$, is anomalous, which puts the "standardness" of the CO bond in question.

Competition between CH and CC bonds in aldehydes is not so strenuous, and for this reason, assuming that for each bond neighboring with a carbonyl one in aldehydes (and ketones) $A'/2 = 0.3\,\pi$, we obtain from formula (7) $l_{CC} = 1.50$, whereas the experimental value for acetaldehyde is $l_{CC} = 1.50 \pm 0.02$.* This explains the fact, which was inexplicable to Welland [2], that shortening of CC bonds occurs when they neighbor on carbonyl bonds, but is absent when they are next to an ethylenic bond.

The shortening of the central CC bonds of glyoxal and diacetyl should be at least twice as great as in acetaldehyde, where $l_{CC} = 1.50 \pm 0.02$. Assuming, however, that as with butadiene [1] the presence of "countercurrent" π-charges causes increase in the π-electron charge of the central bond, at the expense of the vicinal ones (this is confirmed by the finding that the value of l_{CC} is 1.54 ± 0.02 for the CH_3–C bond of diacetyl), we calculate the length of the central bond of diacetyl as being $l_{CC} = 1.40$, whereas the experimental value is $l_{CC} = 1.47 \pm 0.02$. We evidently have here the repulsive effect mutually exerted by the carbonyl groups, which opposes the shortening of the CC bond in glyoxal and diacetyl, and even leads to the lengthening of the CC bond in oxalic acid ($l_{CC} = 1.57$; 1.59). Where there is no electrostatic repulsion, as in benzoquinone ($l_{CC} = 1.50$; $l_{C=C} = 1.32$ and $l_{CO} = 1.14$), there is no anomaly; $S_{CC} + S_{CO} = 8\,\pi$.

Of the scanty data available for polyhydric phenols resorcinol $l_{CO} = 1.36$; 1.37 and $l_{CC} = 1.39 \pm 0.01$ and phloroglucinol $l_{CO} = 1.36$ and $l_{CC} = 1.40$ it seems questionable that the length of the CC bond should remain unchanged, the more so as $A_{CO} = 0.5\,\pi$, as calculated from formula (8).

Formula (11) is not applicable to oxygen-containing compounds with cumulated bonds, similarly to allene. For example, for carbon suboxide ($l_{CO} = 1.20 \pm 0.02$ and $l_{CC} = 1.29 \pm 0.03$) $\Sigma S = 6.4 \pm 0.7\,\pi$ instead of 8π. For keten $H_2C{=}C{=}O$ ($l_{CO} = 1.102$ and $l_{CC} = 1.353$) $\Sigma S = 3.75\,\pi$ instead of $4\,\pi$, assuming that $2A_{CH} = 0.28\,\pi$, as in ethylene and allene. Finally, in the carbonate ion ($l_{CO} = 1.23$),** assuming that its structure is represented by the formula , $3A_{CO} = 4\pi$, instead of 6π. The length of the bond may here be affected by mutual repulsion of oxygen atoms, as the carbonate ion may be regarded as three carbonyl groups having a common carbon atom.

The postulates and methods of calculation presented above can also be extended to oxygen-containing organic compounds containing other elements in addition to carbon and hydrogen. Thus, for methyl chlorocarbonate ($l_{CCl} = 1.74 \pm 0.02$; $l_{CO} = 1.19 \pm 0.03$ and $l_{CO'} = 1.35 \pm 0.04$) $A_{CCl} + A_{CO} + A_{CO'} = 2.4\pi$. For phosgene ($l_{CCl} = 1.74 \pm 0.02$ and $l_{CO} = 1.18 \pm 0.03$) $\Sigma S = 2.1\,\pi$; other data are available for phosgene ($l_{CCl} = 1.68 \pm 0.02$ and $l_{CO} = 1.23 \pm 0.02$), but they lead to practically the same value of $\Sigma S = 2.2\,\pi$, as if the authors of the corresponding papers had been dealing with two electron isomers of phosgene.

CN bond. Similarly as for the CO bond, the standard length of the CN bond was taken as the arithmetic mean of the values of l_{CN} for trimethylamine (1.47 ± 0.02; 1.47 ± 0.01); hexamethylenetetramine (1.47 ± 0.02; 1.48 ± 0.01); methylamine (1.47 ± 0.01; 1.48); N-chlorodimethylamine (1.47 ± 0.02); dimethylamine (1.46 ± 0.03; 1.47 ± 0.02); ethylamine (1.47 ± 0.02), triethylamine (1.47 ± 0.02); and dimethylhydrazine (1.47 ± 0.03). $L_{CN} = 1.47$.

Calculation of specific striction of the CN bond from the data for HCN ($l_{CN} = 1.154$ and $l_{CH} = 1.057$), BrCN ($l_{CN} = 1.158$ and $l_{CBr} = 1.790$) and ClCN ($l_{CN} = 1.163$ and $l_{CCl} = 1.629$) by the formula

$$\Delta_{CN} = \frac{l_{CN} - l_{CN}}{4 - \frac{l_{CX} - l_{CX}}{\Delta_{CX}}}$$

leads to one and the same value for $\Delta_{CN} = 0.10$, which testifies to the good mutual agreement of the numerical values for the specific striction of the CC, CH, CBr, and CCl bonds.

---

* The data for acetone, $l_{CO} = 1.14$ and $l_{CC} = 1.56$, appear very unreliable, in view of this.

** Although the original paper [3] quoted three values for l_{CO} in the carbonate ion ($l_{CO} = 1.23 \pm 0.02$; 1.23 ± 0.02 and 1.26 ± 0.02), it will involve no great error if we take all three as being equal to 1.23, since the calculation of l_{CO} for this ion is only for the purpose of illustration, and also as the value $l_{CO} = 1.26$ applies to a CO bond of which the oxygen takes part in a hydrogen bridge. The fact that lengthening of the bond takes place, with consequent diminution of its π-electron charge as a consequence of participation of its oxygen in a hydrogen bond, is evidence in favor of the π-electron nature of the latter.

Although much more diversity is to be found in the types of bonds of nitrogen-containing than of oxygen-containing compounds, data relating to their interatomic distances are far more scanty. Calculation of the π-electron charge of the CN bond in hydrogen cyanide and cyanogen bromide and chloride, using equation (8), and taking $l_{CN} = 1.16$, gives $A_{CN} = 3.1\pi$. Equation (11) is inapplicable to a number of compounds with the cyanide bond. In methyl cyanide ($l_{CC} = 1.49 \pm 0.03$ and $l_{CN} = 1.16 \pm 0.03$) $A_{CC} + A_{CN} = 3.4\pi$ instead of 4π, but it may here be supposed that, as in the case of dimethyldiacetylene [1], the CH bonds of the methyl group, for the length of which no data are available, also possess certain electron charges. For cyanogen ($l_{CC} = 1.37 \pm 0.02$ and $l_{CN} = 1.16 \pm 0.02$) $\Sigma S = 7.4 \pm 0.5\pi$, instead of 8π, and for hydrogen cyanate ($l_{CN} = 1.19 \pm 0.03$ and $l_{CO} = 1.19 \pm 0.03$) $A_{CN} + A_{CO} = 4.4 \pm 0.5\pi$ instead of 4π. The experimental data obviously require further more accurate work.

Calculation shows that for methyl isocyanide $CH_3{-}N{-}C'$ ($l_{CN} = 1.426$ and $l_{C'N} = 1.167$) $A_{CN} = 0.4\pi$ and $A_{C'N} = 3.0\pi$, and this is further evidence that the C'N bond is closer to a triple than to a double bond, i.e., that methyl isocyanide corresponds not with the formula $CH_3{-}\ddot{N}{\cdot\cdot}\ddot{C}$, but with the formula $CH_3{-}N{\vdots}\ddot{C}$. In methyl isocyanate $CH_3{-}N{-}C'{-}O$ $l_{C'N} = 1.19 \pm 0.03$ and $l_{C'O} = 1.18 \pm 0.03$. Assuming that, as for methyl isocyanide, $l_{CN} = 1.43$, we obtain $A_{C'N} + A_{CN} + A_{CO} = 4.9 + 0.5\pi$ instead of 4π; apart from this, we have here a cumulation of double bonds, which led in the above examples to diminution in the value of ΣS. It is evident that in the given case there are grounds for considering the C'N bond a triple one, and for writing the formula of methyl isocyanate as $CH_3{-}\ddot{N}{\vdots}\ddot{C}{-}O$.

It is probable that the same concept, involving cumulated bonds, applies also to urea ($l_{CN} = 1.37$ and $l_{CO} = 1.25$), in which $A_{CN} = 1.0\pi$ and $A_{CO} = 1.2\pi$ and, consequently, $2A_{CN} + A_{CO} = 3.2\pi$ instead of 2π. The assumption that the π-electron charge of the CN bond of urea is augmented at the expense of unshared electron pairs of nitrogen seems for this reason to be a quite natural one, and a structure of urea involving symmetrical distribution of π-electron charges to a certain extent resembles that of the carbonate ion. The full or partial (possibly proportional to "counter-current" π-electron charges) participation of unshared electron pairs in forming π-electron charges of individual bonds is a conclusion strongly supported by experimental facts. We shall below present fresh examples, relating to nitrogen, for which this phenomenon is especially characteristic, although it also applies to oxygen (as in the case of polyhydric phenols). It is not so clear whether unshared electron pairs of halogens can contribute to π-electron charges of bonds.

The π-electron charge in pyridine ($l_{CN} = 1.37 \pm 0.03$) is $A_{CN} = 1.0 \pm 0.3\pi$, and in pyrazine ($l_{CN} = 1.35 \pm 0.02$) $A_{CN} = 1.2 \pm 0.2\pi$; this is still further evidence of the structural similarity of these compounds to benzene.

Acetamide and pyrrole are typical examples of compounds in which the CN bond is next to a multiple bond. In acetamide ($l_{CC} = 1.51 \pm 0.05$; $l_{CN} = 1.38 \pm 0.05$ and $l_{CO} = 1.28 \pm 0.05$) $A_{CC} + A_{CN} + A_{CO} = 2.1\pi$. In the same way as in acids the π-electron charge is distributed asymmetrically between CC and CO bonds which are next to carbonyl bonds, so in acetamide the greater part of the charge undergoes transfer to the CN bond ($A_{CN} = 0.9\pi$; $A_{CC} = 0.2\pi$). In pyrrole ($l_{CN} = 1.42 \pm 0.02$) $A_{CN} = 0.5\pi$. If we calculate the length of the CN bond, as was done before, we obtain the value $l_{CN} = 1.47 - 0.28 \cdot 0.10 = 1.44$.

In glycine ($l_{CN} = 1.39 \pm 0.2$) $A_{CN} = 0.8\pi$ and in alanine ($l_{CN} = 1.42 \pm 0.03$) $A_{CN} = 0.5\pi$. Before attempting to explain this we should be in possession of more reliable data for the lengths of the CN, CC, and both CO bonds. There are unfortunately no data whatsoever for amino- and nitro-derivatives of benzene from which the drawing of any conclusions could be possible.

NN bond. We have no data justifying the acceptance of any particular length of the σ-bond as a standard one; in hydrazine ($l_{NN} = 1.47 \pm 0.02$) and in dimethylhydrazine ($l_{NN} = 1.45 \pm 0.02$), from which the arithmetic mean $L_{NN} = 1.46$. Spectroscopic determination of the length of the bond in the nitrogen molecule $\ddot{N}{\vdots}N$ $l_{NN} = 1.095 \pm 0.008$ and 1.098, or, in round figures, $l_{NN} = 1.10$.

$$\Delta_{NN} = \frac{1.46 - 1.10}{4} = 0.09.$$

In methyl azide $H_3C{-}\ddot{N}{-}\ddot{N}{\vdots}N^*$ ($l_{CN} = 1.47 \pm 0.02$; $l_{NN} = 1.24 \pm 0.02$; 1.26 ± 0.02 and $l_{NN^*} = 1.10 \pm 0.02$) $A_{CN} = 0.0$; $A_{NN} = 2.3\pi$ and $A_{NN^*} = 4\pi$, whence $S_{NN} = 6.3\pi$, while $n = 6\pi$. In hydrazoic acid ($l_{NN^*} = 1.128$ and $l_{NN} = 1.241$) $S_{NN} = A_{NN} + A_{NN^*} = 2.4 + 3.7 = 6.1\pi$. In diazomethane $H_2C{-}\ddot{N}{\vdots}\ddot{N}$ ($l_{CN} = 1.34$ and $l_{NN} = 1.13$),

$A_{CN} + A_{NN} = 5\pi$, while $n = 6\pi$. It is evident that the CH bonds of this compound have undergone considerable shortening.

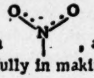
In azobenzenes ($l_{NN} = 1.23 \pm 0.03$ and $l_{CN} = 1.40;\ 1.40;\ 1.43$) $A_{NN} = 2.6\pi$ and (for an arithmetic mean $l_{CN} = 1.41$) $A_{CN} = 0.6\pi$. These results give an indication that the azo-group has the structure $-N\underset{\cdot\cdot}{:}N-$ and hence that an unshared pair (or pairs) of nitrogen electrons participate in the bonds. However, in azomethane ($l_{NN} = 1.24 \pm 0.05$ and $l_{CN} = 1.47 \pm 0.06$) $A_{NN} = 2.4\pi$, and $A_{CN} = 0.0$. Incidentally, these rather old results require checking.

TABLE*

Bond	L	Δ	A
CC	1.542	0.149	±0.07
CH	1.093	0.042	±0.24
CCl	1.779	0.166	±0.06
CBr	1.936	0.16	±0.06
CI	2.132	0.13	±0.08
CO	1.43	0.15	±0.07
CN	1.47	0.10	±0.10
NN	1.46	0.09	±0.11
NO	1.37	0.08	±0.12

NO bond. In the absence of other values the standard length of the NO bond is taken as being that in O-methylhydroxylamine, $L_{NO} = 1.37$. Specific striction of this bond may also be very roughly derived from $l_{NO} = 1.22 \pm 0.02$ in methyl nitrite, since the other NO' and the CO' bonds have the normal values $l_{NO'} = 1.37 \pm 0.02$ and $l_{CO'} = 1.44 \pm 0.02$;

$$\Delta_{NO} = \frac{1.37 - 1.22}{2} = 0.08.$$

Since the length of the CO bond in nitromethane ($l_{NO} = 1.22 \pm 0.02$); methyl nitrate (according to more recent data also 1.22 ± 0.04); and tetranitromethane ($1.22 + 0.02$) is identical with that in methyl nitrite, it is natural to suppose that the structure of the nitro-group is expressed by the formula , and hence that "unshared" electron pairs of nitro-compounds donated by nitrogen participate fully in making up the π-bonds.

Equation (11) is fully satisfied for nitrous oxide ($l_{NN} = 1.126$ and $l_{NO} = 1.191$) $A_{NN} + A_{NO} = 5.95\pi$, whereas in accordance with the formula $\ddot{N}{:}\ddot{N}{-}O$ $n = 6\pi$.

The anomalous length of the bond in trimethylamine oxide ($l_{NO} = 1.44 \pm 0.04$ at $l_{CN} = 1.49 \pm 0.02$; according to older data $l_{NO} = 1.36 \pm 0.03$ and $l_{CN} = 1.54 \pm 0.03$) may be explained as being due to the special ("semipolar") nature of the NO bond in this compound. *

The hypothesis of π-electron distribution thus allows us to combine together and consider from a single point of view the data for interatomic distances in compounds with multiple bonds. In spite of the apparently large amount of such material available, there are serious gaps in the coverage of benzene derivatives (in particular of monosubstituted ones) and of compounds containing nitrogen and iodine, and there are practically no trustworthy data relating to CH bonds. Thus we see that this mass of data was accumulated in a most haphazard manner; one of the virtues of the hypothesis presented by us is that it can be applied to the solution of a number of problems, and can also suggest experimental approaches towards the solution of new problems in the field of interatomic distances, which are of great theoretical importance, and which are ultimately concerned with the elucidation of the electron structure of molecules. In order, however, to assess correctly the cognitive possibilities inherent in the π-electron distribution hypothesis in its present stage, being the initial stage of its development, it is necessary to have a clear picture of the assumptions on which it rests, of the reliability of the basic data, and of the accuracy of the final results of the calculations.

Equation (11) $\Sigma S = n$ may be called an equation of additivity of π-electron charges. If it is satisfied for a compound possessing different types of bonds, such as phosgene or nitrous oxide, or if agreement is obtained for the calculation of specific striction of the CN bond, using this equation, from different independent data, then this should be regarded as being evidence in favor of the truth of the initial hypothesis and of the correctness of the constants L and Δ. Verification of the correctness of equation (11) is unfortunately not possible for a large number of compounds, owing to the absence of data for the CH bond. Cases are, however, encountered in which equation (11) is quite obviously not satisfied (for example, compounds with cumulated multiple bonds $-\ddot{C}-$). The reason is that in establishing a direct proportionality between the magnitude of the π-electron charge and of striction of the bond we deliberately ignored such factors as mutual reactions of π-electrons belonging to one and the same atom, which cannot as yet be considered quantitatively, as well as irregular distribution of π-electron density along the bond, etc. We thus started with the assumption that the basic factor affecting striction of a bond is the magnitude of its π-electron charge, and that all other factors are of only secondary importance. We also postulated that the π-electron charge is confined to the limits of a bond, and that they are distributed in the following way in acetylene:

---

* The values for L and Δ for various types of bonds are reported in the Table in which are reported as well as the values of ϵ_A – the absolute errors in the determination of the π-electron charge, if the absolute error in the determination of the bond length $\epsilon_1 = \pm 0.01$.

$$H \overset{0.86}{\cdots\cdots} C \overset{2.27}{\cdots\cdots} C \overset{0.86}{\cdots\cdots} H,$$

but not, for example, as follows:

$$\alpha + \beta\ H \overset{0.86-\beta}{\cdots\cdots} C \overset{2.27-2\alpha}{\cdots\cdots} C \overset{0.86-\beta}{\cdots\cdots} H\ \alpha + \beta,$$

where α and β are fractions of a π-electron charge, or, at least, that these fractions are so small as to be negligible for the purposes of our calculation. The agreement of most of the data for interatomic distances with the π-electron distribution hypothesis is evidence in favor of the above assumption. The existing exceptions do not invalidate this assumption, since they themselves may in turn be generalized, as in the case of compounds with cumulated multiple bonds, or they may even be explained, in some cases. Thus the greater length of the central bonds than the calculated values, observed in the cases of oxalic acid, glyoxal, and diacetyl, is explained as being due to the mutual electrostatic repulsion of carboxylic and carbonyl groups, and the greater observed than calculated striction of bonds in isocyanides, isocyanates, and certain other compounds, to partial participation of unshared electron pairs in the formation of the π-electron cloud of these bonds. In some cases the experimental data on which apparent exceptions are based may be questioned, such as the interatomic distances in acetone, the length of the hydroxyl bond of CO in acetic acid, the length of the CH_3–C bond in p-xylene, etc.

A reason for the discordance of certain data, and the non-applicability of equation (11) may also be a result of inaccuracies in the results calculated from equations (8) to (10) for π-electron charges, and this, in turn, is a result of inaccuracies in the determination of the magnitudes entering into these equations, such as the experimental values for the length of a bond $\underline{l}$, the standard length of the σ-bond L, and the specific striction Δ. We shall therefore consider the effect of inaccuracies in the determination of each of these magnitudes on the result of calculation of the π-electron charge A by equation (8).

1. Interatomic distances are determined spectroscopically with an absolute error of the order of thousandths of an Angstrom, but these methods are applicable only to the simplest molecules. The authors of papers on determination of interatomic distances by roentgenographic and electronographic methods estimate the absolute error involved at $\epsilon_l = \pm 0.02, \pm 0.03$ and even ± 0.04. In most cases, however, the absolute error indicated in the tables is on the high side, and, in fact, of the nineteen above-quoted values for the length of the unexcited CO σ-bond, as found for a number of compounds, calculations based on the formulas of the theory of mean errors give as the probable error of an individual determination a value of $r_{l_{CO}} = \pm 0.009$. As regards the absolute ϵ_A and the relative δ_A of errors of determination of the π-electron charge, it follows from equation (8) that

$$\epsilon_A = \pm \frac{\epsilon_l}{\Delta}, \text{ while } \delta_A = \pm \frac{\epsilon_l}{\Delta A} \cdot 100\%.$$

It is evident from the above Table, which gives ϵ_A values calculated on the assumption that $\epsilon_l = \pm 0.01$, that the determination of the length of the CH bond has to be performed with particular accuracy. Inasmuch as we possess as yet only isolated measurements of interatomic distances for the vast majority of organic compounds, and hence cannot subject these to the usual mathematical treatment, it is reasonable to take into consideration not the values of absolute errors as given by the authors of the appropriate papers, but the correspondence of data obtained for bonds of one and the same type in structurally analogous members of a series of compounds.

2. For the standard length L of the σ-bond we have taken either the arithmetic mean of a series of values for the lengths of bonds of one and the same type in compounds not possessing multiple bonds, or else we have taken single determinations, usually obtained by the spectroscopic method. The values of L were derived by the former method for CO, CN and NN bonds, and in these cases it is possible to calculate the probable error r_L of the arithmetic mean. We obtained the value $L_{CO} = 1.430 \pm 0.002$ for the CO bond, from the above-cited data, but since, as has been shown above, the probable error of each separate determination of bond length for CO would be $r_l = \pm 0.009$, it follows that the value of L_{CO} should be taken only to the second decimal place. For the NN bond we were obliged to take the arithmetic mean of two determinations only.

Experimental values for the CC, CH, CCl, CBr, CI, and NO bonds were taken for L, by the second method. Here too we took into consideration the arithmetic means, which, for example, coincide for the CC bond with $l_{CC} = 1.542$ in diamond (roentgenographic method), but not with $l_{CC} = 1.573$ in ethane (spectroscopic method).

It should not, strictly speaking, be considered that any given value of L could serve as a standard for σ-bonds of all compounds. Thus the length of the CC σ-bond is different in ethane and in hexachloroethane, and it was hence necessary, in calculating the π-electron charge of ethylene and tetrachloroethylene, to take different values for L_{CC}. In view, however, of the insufficient trustworthiness of the relevant experimental data, and of the absence of even semi-quantitative generalizations relating to the relatively small fluctuations in the length of the σ-bond in saturated compounds, it seemed to me that it would be premature to attempt to introduce the corresponding corrections.

All that we said above regarding inaccuracies in the determination of the length $\underline{l}$ of bonds applies equally to the effect of errors made in determining L on the result of calculating the π-electron charge A.

2. Specific striction Δ can be either calculated independently, as has been done above for the CO and NN bonds, or else, as in most cases, it can be derived from equation (11), as for CC and CH bonds [1]. Calculation of Δ_{CCl}, Δ_{CBr} and Δ_{CI} was made by means of equations containing the terms Δ_{CC} and Δ_{CN}, from equations containing the terms Δ_{CH}, Δ_{CBr} or Δ_{CCl}. Whichever method of calculation is used, the trustworthiness of the values for the standard length L of the σ-bond and of the experimentally determined values $\underline{l}$ of bond length are of great importance for the calculation of specific striction. The value of $\underline{l}$ is selected from individual results (mostly spectroscopic) for simpler compounds (acetylene, ethylene, dichloro-, dibromo-, and diiodo-ethylene, carbon monoxide, hydrogen cyanide, etc). As has already been said, the selection of carbon monoxide for calculation of Δ_{CO} cannot be accepted without reservation. Inaccuracies in the determination of data for ethylene, in particular for its CH bond,* may be the most serious source of error in calculating specific striction of a whole series of bonds, since any such inaccuracies are multiplied by 4 in the process of calculation.

Without doubt sufficiently trustworthy values will with time be available for $\underline{l}$, L, and Δ, but until then the values calculated from equations (8) to (10) can only be regarded as giving a semi-quantitative, or even only a qualitative, picture of distribution of π-electron density among the bonds of organic compounds. It will in time be possible to define more narrowly the limits of applicability of the basic hypothesis, and to explain the observed deviations from them. Even now, however, the π-electron distribution hypothesis can be applied to the explanation or even to the calculation of certain properties, chiefly additive ones, of organic compounds, giving additional quantitative material relating to distribution of π-electron charges on different types of bonds in molecules; as will be shown by me in future papers this possibility is quite a real one. The π-electron distribution hypothesis thus promises to become a step forward towards the formulation of a semi-quantitative theory of the electron structure of chemical compounds. Further steps along this path will be the study of the relation between the π-electron density distribution and the physical properties of a substance, the application of the methods elaborated to the study of σ-electron density distribution, the establishment of the laws governing reaction and mutual transformation of π- and σ-electron densities, the elucidation of the electron mechanism of mutual reactions between atoms, and the broader understanding of the chemical properties of molecules.

SUMMARY

1. The π-electron distribution hypothesis has been extended to organic compounds containing the CCl, CBr, CI, CO, CN, NN and NO bonds.

2. The reliability of the basic data and of the final calculated results for π-electron charges of bonds are discussed.

Received December 10, 1951

LITERATURE CITED

[1] G. V. Bykov. Bull. Acad. Sci. USSR, (Div. Chem. Sci., No. 6, 823 (1951).

[2] G. Welland. Theory of resonance, and its application to organic chemistry, p. 157. GIIL, Moscow, 1948.

[3] C. J. Brown, H. S. Peiser and A. Turner-Jones, Acta Cryst. 2, 167 (1949).

---

* Apart from the values (l_{CC} = 1.330 and l_{CH} = 1.087), used for the calculation of Δ_{CC} and Δ_{CH} [1], we also have other data for this compound (l_{CC} = 1.353 and l_{CH} = 1.071), which we do not take into consideration, since calculation of specific striction in the way applied in our first paper leads to obtaining negative values of Δ_{CH}, which is obviously absurd.

BLANK
PAGE

CHRONICLE

240TH ANNIVERSARY OF THE BIRTH OF M. V. LOMONOSOV

The Division of Chemical Sciences, Academy of Sciences USSR, held a session on the 27th of November, 1951, in honor of the 240th anniversary of the birth of that great thinker and propangandist, the brilliant founder of Russian science, Mikhail Vasilievich Lomonosov.

Opening the session, Academician-Secretary of the Division of Chemical Sciences of the Academy of Sciences USSR, Academician M. M. Dubinin said: "The Soviet Union looks back with pride at the path traversed by Russian science from Lomonosov's time to the present day. This path was marked by great discoveries and achievements. Lomonosov's scientific heritage is many-sided, for he preceded the development of progressive natural scientific thought of our era. Russian chemical science has progressed to its present great successes from Lomonosov through the great chemist Butlerov and the founder of the periodic system, Mendeleev.. To Lomonosov we can trace the origin of physics, chemistry, mineralogy, geography, astronomy, metallurgy, linguistics, and literature".

Academician Dubinin pointed out that Lomonosov, by raising Russian science to the summits of knowledge, thereby raised the honor and glory of the Russian nation to an unattainable level. His genius, his devotion to his country and his nation, his uncompromising attitude towards the enemies of Russia, and his untiring energy are to us citizens of the great Soviet Union a great and inspiring example of endeavor for the good of our Fatherland.

Academician A. V. Topchiev said in his lecture: "M. V. Lomonosov – the great Russian Scientist", the creative work of M. V. Lomonosov provides striking evidence of the genius of the Russian nation, which has achieved its full development during the Stalin epoch. Lomonosov's character was influenced by his Russian national milieu, by the way in which the country itself was then developing, by the special peculiarities of the technical and social development of North Russia, which had not known the Tartar yoke or the oppression of the nobles.

Lomonosov's life-story is one of unremitting struggle for possession of knowledge, for the approach of knowledge to objective, absolute truth, against a clique of enemies of Russian science, against bureaucratic control of the Academy of Sciences, against the adoption of a servile attitude towards foreigners, against the depreciation of Russian science. His one regret, when on his death bed, was that he had not been able to achieve all that he had undertaken for the good of his country, and that with him would perish all his useful projects.

"But", continued A. V. Topchiev, "Lomonosov's useful projects did not perish. His brilliant concepts, ideas, and discoveries have become the basis of present-day science. The ideas of the conservation of mass and of energy, of atomistics, of the origin of the world and of the universe expressed by Lomonosov two centuries ago are the basic ideas of modern physics, chemistry, and geology".

The diversity of Lomonosov's work was so great that his Western contemporaries who read his odes and poems, and his scientific works on astronomy, geography, and metallurgy were convinced that these were produced by different authors. S. I. Vavilov wrote the following in a paper describing the diversity of Lomonosov's creative thought: "The great Russian encyclopedist had in fact a coherent and monolithic nature". Lomonosov was the most prominent materialist philosopher of his period. His materialistic views formed the basis of all his naturalistic papers.

Lomonosov's first scientific works, written in 1741-1746, and in particular his letters to Euler, contained the clearly expressed ideas of the conservation of mass and motion. S. I. Vavilov wrote in his articles on Lomonosov that "Lomonosov was a century ahead (of his contemporaries) in bracketing, as it were, all forms of conservation of properties of matter, the most profound content of the great natural law. . ." It was in Lomonosov's works that the idea of conservation of mass was first announced, with exceptional clarity, and was made the basis of the elucidation of the most important physico-chemical problems. A. V. Topchiev regards the creation of the fundaments of scientific atomistics as being one of the great scientific advances due to Lomonosov.

"Lomonosov was the first of the thinkers of his time", continues A. V. Topchiev, "to form a consistent picture of nature, based on atomistic principles, and he creatively applied atomistic concepts to the solution of the most important problems of science—to the structure of substances, to the discovery of the nature of chemical reactions, and to the analysis of the laws of heat, of atmospheric electricity, etc."

Lomonosov believed that bodies consisted of corpuscles, which in turn contain a certain number of "elements", "insensitive particles". Lomonosov's "corpuscles" are molecules, and his "elements" or "insensitive particles" are the atoms of modern chemistry. Lomonosov's chemical atomistics were the foundation of all his gigantic theoretical and experimental work, which initiated the basic trends of modern scientific chemistry.

His physical researches were all connected basically with atomistics, from which standpoint he approached the problems of heat, gravity, light, and electricity. He combined brilliantly a talent for experimentation with a capacity for profound theoretical thought. He was the founder of Russian natural history. The chemical laboratory founded by him in the Academy of Sciences was a first class research establishment, and in it he created and developed a new science—physical chemistry, which followed from his atomistic views. He wrote: "Physical chemistry is a science which explains, on the basis of physical concepts and experiments, processes taking place in mixed bodies by means of chemical operations", and, further, that he wished to "investigate all that can be measured, weighed, or determined by calculation". Lomonosov's experimental work led him to the law of the conservation of matter; this discovery has for long been credited to Lavoisier, who, however, only repeated Lomonosov's experiment 17 years later, without drawing the necessary conclusion from the result. Soviet research workers have shown that the priority for this discovery belongs properly to Lomonosov, with whose work Lavoisier was acquainted, and, further, that Lavoisier did not in his publications usually refer to the original sources.

Lomonosov's talents were many-sided, and his activities were most diversified. His chemical researches were closely connected with the Russian mosaic industry. His ideas, and his powerful urge towards practical work found their expression in geological work, in prospecting for and utilization of the limitless mineral wealth of Russia, in the study of the geography of Russia, in plans for the conquest of the Arctic, and in the organization of Arctic expeditions. Lomonosov's astronomical works combine practical application with breadth of philosophical generalizations. "Lomonosov's poetyr", continued Topchiev, "is immortal, for the profundity and boldness of its scientific ideas, for its merciless opposition to reactionary forces, and for its patriotic love of his Fatherland".

Lomonosov endeavored in his poetry to inculcate a new attitude towards science, as well as to popularize new ideas throughout Russia. Before his time there was no grammar, no one took any interest in stylistic purity. Having come to the conclusion that the latter depends above all on "a thorough knowledge of the language", he undertook the compilation of his "Russian Grammar". This was the first really scientific work on the Russian language; its role was of particular interest in the light of Stalin's brilliant works on linguistics. The heritage of Lomonosov is indeed a great one; all his work was permeated by patriotism, by love for his country. The Soviet people honor the memory of the great men of the past, who under difficult conditions created the scientific and artistic treasures of the nation.

Professor N. A. Figurovsky then read a paper on Lomonosov's chemical works, and on their significance for the development of science. He said that it was only with the beginning of the present century that proper interest began to be taken in Lomonosov as a scientist, although Russian scholars, men of letters, and philologists had for two centuries studied with profound interest the personality of this remarkable man. Most of the materials relating to the activities of Lomonosov have now been published, but the study of his work, his role as the founder of science in our country, is only now beginning. His ideas and theories have inspired many important trends in the development of chemistry at least a century before they materialized. Lomonosov's slogan: "A real chemist must be a theoretician and a practical man" is particularly well understood and valued by Soviet scientists, who are participants in the great public works of Communism.

M. V. Lomonosov—atomist and research worker. His atomistics was at the core of all his theories; as a real revolutionary of science he made use of every possibility, he drew logical conclusions, and gave explanations of the most varied phenomena. In his thesis: "Elements of mathematical chemistry" he first gave his definition of chemistry, as the science relating to changes taking place in compound bodies, starting from the proposition that in "mixed bodies" (i.e., compound ones) all changes depend on changes in their internal qualities. The factors determining the internal qualities resided, in his opinion, in the properties of the particles of which the bodies are made. All bodies consist of atoms, which were then called elements. "An element is a part of a body not consisting of any other smaller bodies which differ from it". Aggregations of elements were called "corpuscles" – in modern terminology, molecules. Lomonosov distinguished between homogeneous and heterogeneous corpuscles; "corpuscles are homogeneous if they consist of identical numbers of identical elements, joined to each other in the same way", wrote Lomonosov. "Corpuscles are heterogeneous when their elements are different, and are present in different numbers and are joined to each other differently; on this depends the infinite diversity of bodies." No one had before Lomonosov so definitely spoken of the existence of molecules of simple substances. The incorrect formulae assigned in the first half of the 19th century were due to lack of clarity regarding the nature of molecules of simple substances. The most complete confusion reigned regarding the concepts: atom, atomic weight, molecule, molecular weight, equivalent. It was not until 1860 that an international conference established order in the domain of precise definition of concepts and views first expressed by Lomonosov in 1741. Thus Lomonosov formulated the basic postulates of the atomic-molecular teaching 120 years before they were officially acknowledged.

Lomonosov realized the importance to science of the atomic theory at a time when even to dream of its direct proof was impossible. In his paper "Attempt at a theory of insensitive particles of bodies and in general of causes of qualities" certain aspects of the atomic-molecular theory are discussed in detail and extended, with particular respect to the mutual attraction of insensitive particles, and to the presence within them of forces of inertia.

Lomonosov's work "Thoughts on the causes of heat and cold" was a further step forward towards the development of progressive materialistic thinking. At a time when belief in fire material – "imponderable fluids" – was prevalent, Lomonosov took the unusual viewpoint for his times that "An adequate basis for heat is to be found in motion.....And since motion cannot exist without matter, it follows that the basis of heat is to be found in the motion of some material". He puts this more precisely as follows: "heat consists in the internal motion of matter". Thus we see that Lomonosov made an important logical conclusion as to the nature of heat, based on his atomic-molecular theory.

Lomonosov may be said to have formulated the fundaments of the molecular-kinetic theory. He postulated the existence of the absolute zero of temperature, as well as the absence of an upper limit of temperature. He repeated Boyle's experiments on the calcination of tin and lead, and demonstrated the importance of air in these experiments. His conclusions as to the mechanical theory of heat are of interest, as are those relating to phenomena of heat exchange between heated bodies: "... a cold body B immersed in a substance A can obviously not acquire a greater degree of heat than that which A has". This paper created a sensation among the ignorant foreign academicians.

Lomonosov explains, in a letter to Euler, that matter is inseparable from motion, and further develops his law of the conservation of matter and energy. The idea of the conservation of force and motion is a logical consequence of the whole complex of materialistic world outlook adopted by Lomonosov. His law is no chance remark – it is an essential part of his natural philosophy, an indispensable link of his scientific materialistic system. N. A. Figurovsky points out that it is to Lomonosov that we owe the discovery of those two great laws of nature, the law of conservation of matter and the law of conservation of energy.

Lomonosov's words resound with exceptional strength in the wonderful epoch of Stalin: "Chemistry spreads her arms widely over the affairs of men. Wherever we look, wherever we turn, we see before our eyes evidence of its successful application". Our primary task is to develop the successful applications and achievements of chemistry.

Corresponding Member of the Academy of Sciences I. N. Plaksin, in his address on "M. V. Lomonosov – founder of scientific metallurgy", spoke of the Russian "ore-experts", "prospectors", "miners", and "smiths" who laid the foundations for the further development of Russian ore mining and metallurgical industries, the inception of which belongs to a remote period of history. The smelting of iron began in 1701 at the Kamensk and Nevyansk Works, and during the following years more than 20 iron refining and 60 copper smelting furnaces were built. Russia led the world in copper production in the first half of the 19th century. The Russian cast-iron and iron industry was of world-historical importance, and it had a considerable effect on the industrial revolution in England. The development of industry in Russia was based on the accumulated experience of centuries.

The speaker showed that Lomonosov took the first place in the creation of the scientific fundaments of metallurgy. He wrote in 1755: "...the openings of the interior of the earth...from them pour metals, which are plentifully distributed not only throughout our native land, but also to foreign nations. The heroic Russian army directs against the enemy weapons forged from Russian minerals by Russian hands".

Lomonosov's work "Fundamentals of metallurgy for ore workers", published by the Academy of Sciences in 1763, laid the scientific foundations of a number of geological, mining and metallurgical disciplines. The book received a wide circulation, and for over a century and a half it served as a practical manual for workers in the metallurgical industry. In contra-distinction to his other scientific works, which were not understood or appreciated by his contemporaries, Lomonosov was rewarded for this book by a special edict of the Empress Catherine II, his salary as a Civil Councillor being raised to 1875 roubles per annum.

According to Lomonosov theory and practice must constantly be correlated. "From observation to establish theory, through theory to put observation on the right track – this is the best of all ways of seeking the truth". He wrote that "a chemist should not be the sort of person who has gained his knowledge from the study of books only, he should have convinced himself by his own efforts of the truth of this knowledge", but at the same time he warns the student against an attitude of primitive empiricism.

Lomonosov's way of presentation was that of a real scientist, who works with a definite end in view, who does not lose sight of this end, and who maintains a rigorous scientific discipline in his thinking. Lomonosov's book, in which he presents the system of Russian scientific chemical terminology created by him, is one of the most remarkable books in the history of metallurgy, chemistry, and mining, for the novel and orderly way in which it is written.

In 1777, however, 12 years after Lomonosov's death, a slanderous anonymous article was published, announcing that this book was in fact only a translation of a book written by the director of the Nieder Hartz Metallurgical Works, one Schluetter; later historians of science (Academician V. I. Vernadsky, 1900) showed that these books have nothing in common. Schluetter's book contains 612 + 198 pages and 58 Tables, and it describes metallurgical practice in the Works under his control, whereas Lomonosov's book consists of 12 + 416 pages and 7 Tables, and it expounds the essentials of metallurgical industry, and also gives practical instructions. He shows in the preface how certain authors had uncritically copied information on the preparation of ores from other works, and he gives in his book a unitary system of metallurgical procedure.

I. N. Plaksin concluded with a description of the contributions made by Russian metallurgical chemists to the science of metallurgy, which were particularly numerous during the Stalin Five Year Plans.

Corresponding Member of the Academy of Sciences K. A. Kocheshkov presented to a meeting of the Division of Chemical Sciences of the Academy a paper written jointly with Candidate of Chemical Sciences E. M. Panov on "A new class of simple organic compounds of lead", on the 28th of November, 1951. The speaker reported that they had synthesized 7 representatives of a new class of metallo-organic compounds of elements of the IV Group of the periodic system, of the general formula $ArPbX_3$, by a very simple method.

Salts of lead organic acids were taken for the syntheses, which gave many advantages. The paper gave a detailed description of the new class, presented evidence of the structure of the compounds, and described a number of reactions given by them. It was shown for the first time that the reaction of dearylation of compounds of the class Ar_4Pb may proceed with elimination of three radicals, to give lead organic compounds in which lead is combined with only one aromatic radical.

The compounds of the new class give the usual reactions of lead organic salts. Addition of dilute alkalis or of aqueous ammonia to alcoholic solutions of phenyl-lead triisobutyrate gives a precipitate of the hitherto unknown phenylplumbic acid. The authors synthesized 5 new compounds of the class Ar_2PbX_2, and physical constants were determined for 3 of them. Lead organic compounds of the p-tolyl series of the class $ArPbX_3$ were synthesized.

Corresponding Member of the Academy of Sciences V. I. Spitsyn read a joint paper with L. D. Kolli, entitled: "Study of the processes of dehydration and thermal decomposition of certain heteropoly-compounds". These compounds are distinguished by a high water content, and little is known of the way in which this is bound. The paper reports the results obtained using a modified MacBain balance for the process of isobaric dehydration of lithium, potassium, and calcium silicotungstate and of potassium phosphotungstate and phosphomolybdate, at 25-600°. The results showed that in heteropoly-compounds containing phosphorus residual water is held much more firmly than in the case of those containing silicon. Replacement of potassium by lithium or calcium, the ions of which have a more powerful polarizing action, leads to weakening of binding of water. The amount of residual, most firmly bound, water in the silicon compounds studied is 0.5 mol, and in the phosphorus compounds 1 mol per atom of complex forming element. This effect corresponds to 1 or 2 hydrogen atoms being in a special position in the coordination structure, possible in the complex nucleus of the compounds.

The action of water on the residues obtained by calcination of the heteropoly-compounds was also studied. Lithium silicotungstate gives an insoluble residue when heated at 200°. Potassium and calcium silicotungstates are partially decomposed at 300°, and sodium phosphotungstate is decomposed only at more than 300°.

The aqueous extracts and the calcined residues were analyzed. Thermal decomposition of alkali metal salts of silicon-containing heteropoly-compounds gives a soluble silicate, and not silica, whereas phorphorus-containing compounds yield soluble alkali metal phosphates under these conditions. It is evident that these reactions result from an appropriate position of the silicon, and also of the phosphorus, atoms in the compounds, and it is very probable that the position of silicon or phosphorus in the coordination nucleus of the heteropoly-compounds in relation to the cation of the outer sphere is to a certain extent approached to that of tungsten and molybdenum.

BLANK
PAGE

AWARD OF D. J. MENDELEEV PRIZES FOR 1951

The Praesidium of the Academy of Sciences USSR has awarded D. I. Mendeleev prizes for 1951, for the following works.

Prizes of Rb. 20,000 each

1. To Doctor of Chemical Sciences A. V. Kirsanov for his series of papers "Researches on the transformation of sulfanilic acid, and syntheses performed with sulfanilamide".

2. To Candidate of Physico-Mathematical Sciences Yu. N. Ryabinin for his paper "On certain properties of dense gases".

Prizes of Rb. 10,000 each

1. To Doctor of Chemical Sciences A. V. Kiselev for his paper "Structure of adsorbents and energy of adsorption".

2. To Doctor of Chemical Sciences A. I. Shatenshtein for his papers "Theory of acids and bases", "Comparison of the strength of very weak acids", and "Studies of isotope exchange in liquid deutero-ammonia".

A. V. Kirsanov's series of papers on the reaction between sulfanilic acid and phosphorus pentachloride, and on the study of the properties of trichlorophosphazosulfuryl chloride formed therefrom, is an orginal and productive research. He showed that previous workers had been mistaken, and that the product was in reality the chloride of trichlorophosphazosulfuric acid, and not a complex of sulfanilic acid with phosphorus trichloride, as had been believed before. Kirsanov established the structure proposed by him by means of scrupulous analyses and by study of its properties.

A. V. Kirsanov extended the reaction discovered by him to the study of the reaction of arylsulfanilamides with phosphorus pentachloride, and found that the products are trichlorophosphazosulfonaryls; the structures suggested for these products by earlier workers are mistaken. Kirsanov studied the reaction of thermal decomposition of the chloride of trichlorophosphazosulfuric acid, with the object of obtaining an interesting product, viz., that obtained by elimination of PCl. A series of trimers of this product were obtained, and it was named sulfanuryl chloride, by analogy with cyanuryl chloride. Kirsanov then presented the results of research on the so-called imidosulfanilamide (hydrolysis, methylation, etc.), leading to the elucidation of its structure and properties. One of the interesting applications of the reaction described by Kirsanov is his new method for preparation of nitriles of carboxylic acids by the use of trichlorophosphazosulfonearyls.

Kirsanov's work is of a high scientific level, and was done with much skill.

Yu. N. Ryabinin's paper "On certain properties of dense gases" is an experimental study of the properties of certain gases (air, nitrogen, argon) adiabatically compressed at pressures of the order of tens of thousands of atmospheres. He was able to perfect known methods of adiabatically compressing gases at these ultra-high pressures, and he describes a reliably working equipment for the study of gases at pressures of 10,000 atmospheres and at temperatures of about 9000° attained during adiabatic compression. This apparatus permitted of the measurement of the volume and pressure of adiabatically compressed gases, of the study of their optical properties, of the measurement of their electrical conductivities, and of the study of chemical reactions (oxidation of nitrogen) taking place in adiabatically compressed air. The author found that at high pressures distribution of energy at different frequencies follows Wien's law. This made it possible to determine the temperature of the compressed gases.

Electroconductivity measurements showed that adiabatically compressed air is ionized, and is therefore a super-dense plasma. It was shown that at voltages of 30-17, 800 V/cm the electroconductivity of the gas is of an ohmic nature. It was also found that in gases of very high density the ionization potential is lowered in comparison to that of an isolated atom, and an explanation of this phenomenon is given. Ryabinin found further that the adiabatically compressed gases obey the ideal gas equation. Although this finding is not an unexpected one, in view of the very high temperature developed during the adiabatic compression of gases, Ryabinin was the first to confirm this quantitatively.

His studies of the oxidation of nitrogen during adiabatic compression of air are of considerable scientific importance. Ryabinin's work has resulted in the opening up in the USSR of a new domain of study — that of physical and chemical phenomena in adiabatically compressed gases. These important studies have contributed to the extension of our knowledge of the condensed state of matter. Thanks to them world scientific literature has for the first time received information on the properties of gases at super-high pressures and at very high temperatures.

A. V. Kiselev's paper "Structure of adsorbents and energy of adsorption" is an outstanding experimental and theoretical study, being a striking concrete example of the superiority of Soviet over foreign science. The original theoretical parts of the paper are those concerning an adsorptional-structural method of study of highly disperse and porous bodies, with, as a general conclusion, the concept of structural types of adsorbents. Of considerable importance is the theoretical analysis of the effect of adsorbent structure on the shape of the isotherms, and also of the stratification taking place in the gaseous or liquid phase in contact with the adsorbent. The new phenomenon of capillary stratification in adsorption from solutions was not only predicted theoretically but was also demonstrated experimentally, and was studied in detail. There is also much original thought in the "thermodynamics of adsorptional processes" developed by the author.

One of the most important of Kiselev's experimental achievements is the design of a precision adsorptional calorimeter with constant heat exchange, and with a temperature sensitivity substantially exceeding that of any known calorimetric apparatus. A very broad and systematic survey was made of different adsorbents belonging to various structural types, and it yielded quite important results. Absolute values for adsorption and for energy of adsorption, both per unit area of adsorbent, were for the first time measured and compared for porous and non-porous adsorbents. Of considerable theoretical and practical significance are the researches on poisoning and regeneration of silica gel surfaces in adsorption of methanol, shown to be due to formation of surface ethers.

The systematic application of the adsorptional-structural method to the most diverse adsorbents led to the obtaining of very valuable results, of immediate practical applicability. A detailed analysis of the processes of multimolecular adsorption and of capillary condensation was made, on the basis of the experimental results for the adsorption isotherms and the differential heat of adsorption.

A. I. Shatenshtein's monograph "Theory of acids and bases" presents the history of the development of the theory of acids and bases, and gives a detailed critical review of contemporary theories. The outstanding role played by Russian scientists in the development of the progressive theoretical treatment of the subject is shown.

The evaluation and criticism of contemporary theories are based largely on the experimental work of the author, consisting of studies of solutions in non-aqueous solvents, chiefly liquid ammonia and sulfur dioxide; the most important results of this work are given in a summarized form in the monograph.

The author gives a comprehensive picture of acid-base equilibria in liquid ammonia, this being of fundamental importance for the theory of protolytic acid-base equilibrium, since liquid ammonia is one of the most protophilic solvents known. Differences between the strengths of strong acids disappear in liquid ammonia, and the strength of weak acids rises sharply, thus making it possible to compare the acidity of substances which do not display acidic properties in aqueous solution.

The results obtained are also of interest for the theories of solutions and of homogeneous catalysis, since they include the first quantitative data obtained for acid catalysis and for salt effect in liquid ammonia. Owing to the low dielectric constant of the solvent, ionic association takes place in even quite dilute solutions, and the velocity and energy of activation of the reaction of ammoniolysis depend not only on the charge but also on the radius of ions of acids and salts present in the solutions.

The researches on solutions in liquid sulfur dioxide allowed the author to formulate a concept of aprotonic, acid-like substances which can, similarly to acids, take part in equilibria with bases.

The study of weak acids was continued in the paper "Comparison of the strength of very weak acids", the results of which were presented in a more detailed form in the article "Researches on reactions of isotope exchange of hydrogen in liquid deutero-ammonia". The measurement of the velocity of exchange reactions of hydrogen isotopes in this medium is suggested as a quantitative method for comparison of the lability of hydrogen in different hydrocarbons. The importance of this method extends beyond the limits of the theory of acids and bases; it opens the way towards the achievement of new results of interest to theoretical organic chemistry.

The work of A. I. Shatenshtein is an important contribution to the theory of acids and bases, as well as to the theory of reactivity of organic compounds. It opens up wide perspectives for the making of further generalizations, and for the obtaining of new data of importance to theoretical organic chemistry.

BLANK
PAGE

BLANK
PAGE

ELECTROCHEMICAL BEHAVIOR OF IRON IN OXIDIZING MEDIA

COMMUNICATION 3. CATHODIC POLARIZATION OF IRON IN OXIDIZING MEDIA

L. Ya. Gurvich and G. V. Akimov*

The cathodic polarization of iron has been the object of a number of investigations. In a study of the cathodic polarization of iron in a buffered solution in an atmosphere of air and oxygen, Tomashov [1] found that the value of the limiting diffusion current was proportional to the partial pressure of oxygen. In an investigation of the cathodic polarization of copper in H_2O_2 solutions of varying concentration, Tomashov again found a linear relationship between the limiting diffusion current and the H_2O_2 concentration. Glasstone and Hickling [2] point out that the limiting current is proportional to the concentration of depolarizer when the processes are reversible, but for irreversible processes it is proportional to $\underline{c}^n$, where $\underline{c}$ is the concentration of depolarizer and $\underline{n}$ has a value between 0.6 and 1.

Krasilshchikov [3] has carried out an investigation of the cathodic behavior of iron in a number of solutions, including oxidizing media: KNO_3 and $K_2Cr_2O_7$ solutions. He found that increase in concentration of KNO_3 from 0.1 N to 1.0 N causes a displacement of the curves in the region of the ionization of oxygen in the direction of more positive values; in the region of hydrogen evolution, the curves for 0.1 N and 1.0 N are practically coincident. We have carried out an investigation of cathodic polarization in solutions of KNO_3 and HNO_3 in the concentration range 0.0001 N – 0.1 N and in 0.1 N solutions of $K_2Cr_2O_7$, $KMnO_4$, and $(NH_4)_2S_2O_8$ (see Table).

The preparation of the electrodes consisted in polishing on abrasive cloth – successively from coarse to finer grades (6/0) – washing with water, and degreasing with alcohol. The electrodes were cylindrical, having a base diameter of 55 mm, and they were cemented into glass jackets by means of Bakelite, as described in Tomashov's book. The potentials were measured on a potentiometer with the aid of a calomel electrode (saturated KCl). The arrangement was shown diagrammatically in our previous communication (4).

In our investigation of the cathodic behavior of iron in 0.1 N and 1.0 N KNO_3 solutions, we have not found the concentration of this oxidizing agent to have an appreciable effect. As Fig. 1 shows, the return branches of the cathodic polarization curves are almost straight lines for high current density in the region of the hydrogen overvoltage. On the return branches, there are no inflections characteristic of the diffusion region. When the current has been cut off, the potential is found to be greatly displaced towards the negative side. The cathodic current evidently removes an oxide or adsorbed film, which, on reduction of the current density (partially, or even to zero), is not reformed in the solution under investigation during the time of measurement.

A cathodic curve determined when the solution is being stirred passes lower than the curve for the still solution. The diffusion region is then moved in the direction of greater current densities. The region of hydrogen evolution on the curve for a moving liquid begins at higher current densities than on the curve for the still solution. The return branch of the curve is displaced with respect to the outward branch in the diffusion and oxygen-ionization regions in the direction of more positive potentials; this was observed also by Tomashov for the cathodic curves given by the solutions investigated by him. The final potential obtained after cutting off the current is more negative than the original potential. The difference between the initial and final potentials in a moving electrolyte is much less than in a still one (in the first case 300 mv, in the second case less than 100 mv). It is evident that

---

* With participation of T. M. Samet.

TABLE

Cathodic Polarization of Iron in Various Media (electrode potential values are given in mV on the hydrogen scale)

Solution	Current density (amp/sq.cm)									
	without current		$2\cdot10^{-6}$		$5\cdot10^{-6}$		$1\cdot10^{-5}$		$1\cdot10^{-4}$	
	initial	final	outward path	return path	outward path	return path	outward path	return path	outward path	return path
0.1 N KNO_3	−145	−570	−310	−645	−540	−690	−715	−725	−845	−720
0.1 N KNO_3 with stirring	−25	−118	−135	−100	−175	−155	−220	−210	−465	−450
1 N KNO_3	−170	−643	−320	−890	−450	−720	−600	−725	−760	−780
			−260		−615		−720		−810	
0.0001 N HNO_3	−190	−438	−435	−640	−600	−675	−715	−715	−800	−710
0.001 N HNO_3	−375	−600	−400	−645	−560	−690	−725	−720	−830	−830
0.01 N HNO_3	−332	−771	−330	−580	−385	−645	−385	−735	−705	−810
0.05 N HNO_3	−302	−307	−310	−295	−310	−295	−315	−295	−365	−315
0.1 N HNO_3	−280	−292	−225	−265	−230	−270	−235	−265	−255	−275
0.1 N KNO_3 0.01 N $Fe(NO_3)_3$	−370	−668	−400	−710	−620	−740	−725	−765	−875	−875
0.1 N $K_2Cr_2O_7$	+200	+137	−335	−385	−550	−515	−625	−575	−960	−900
0.1 N $KMnO_4$	+615	+565	+560	+540	+520	+190	+380	+460	+250	+250
0.1 N $(NH_4)_2S_2O_8$	−287	−300	−300	−300	−300	−300	−300	−300	−300	−300
0.1 N $(NH_4)_2S_2O_8$ 0.1 N NH_4OH	−331	−234	−330	−340	−330	−345	−325	−350	−605	−565

stirring makes it possible for the film to be regenerated, owing to the intensified supply of oxidant.

At the beginning of the region of hydrogen evolution, at a current density of $1\cdot10^{-5}$ amp/sq.cm, the electrode potential is −775 mV. The equilibrium hydrogen potential in neutral solution has the value −414 mV. The overvoltage of hydrogen is therefore 361 mV. At this current density, Frumkin found a value of 0.35 V for the overvoltage of hydrogen at iron [1].

In order to elucidate the part played by depolarization with participation of NO_3' ions, we determined the cathodic curve for iron in 0.01 N HNO_3, with an addition of urea (2 g per liter of solution) (Fig.2). Addition of urea must slow down the depolarization process, which corresponds to the reaction $NO_3' + e = NO_2'$, for urea destroys the NO_2' ions, which act catalytically on this process. As Fig.2 shows, urea has no appreciable influence on the cathodic curve for iron in 0.01 N HNO_3, and consequently, depolarization by NO_3' ions does not play any significant part.

The introduction of KNO_2 into 0.01 N HNO_3 (0.75 g per liter of solution) does not permit the depolarizing role of the ions + NO_2' to be ascertained, for the effect of the NO_2' ions goes beyond the limits of catalytic acceleration of depolarization by the aid of NO_2' ions. KNO_2 acts as a depolarizer on its own account, and it greatly displaces the initial electrode potential of iron to the positive side and changes the course of the cathodic curve.

In order to ascertain the effect of iron ions formed in the corrosion process, the cathodic curve of iron was determined in 0.1 N KNO_3 with the addition of 0.01 g-equiv of $Fe(NO_3)_3$ per liter of solution. It was found (Fig.1) that, while displacing the initial potential of the iron in the negative direction, the Fe^{3+} ions did not alter the essential picture of the cathodic polarization of iron. The hydrogen overvoltage in a solution containing Fe^{3+} is somewhat higher than in pure 0.1 N KNO_3 (by approximately 50 mV). After the experiment, flocs of $Fe(OH)_3$ were to be found in the cathode space. This may have been due to evolution of hydrogen at the cathode with a corresponding increase in the concentration of OH' until the solubility product of $Fe(OH)_3$ was reached. It is possible also that the precipitation of $Fe(OH)_3$ was due to coagulation of its colloidal solution at the cathode.

$1 \cdot 10^{-3}$		Current density at which gas evolution begins	Appearance of Electrode after Test
outward path	return path		
−930	−930	$1.04 \cdot 10^{-3}$	Electrode surface glistening; thin yellow spots at edges.
			Yellow spots in places on glistening electrode surface.
−840	−840		No change.
		$1.3 \cdot 10^{-4}$	Surface of electrode light-colored and glistening.
		$1.7 \cdot 10^{-3}$	Electrode surface gray; dark spots in places.
−980	−960	$1.1 \cdot 10^{-3}$	Darkening of electrode surface; insignificant pitting.
−960	−900	$9.6 \cdot 10^{-3}$	Uneven layer of black and yellow corrosion products on the electrode surface. Electrolyte had become deep yellow.
−335	−335	$7.1 \cdot 10^{-4}$	A black readily removable film on the electrode; the surface under this corroded; electrolyte greenish yellow.
−920	−930	$1.3 \cdot 10^{-3}$	Electrode unchanged; precipitate in electrolyte.
		$4.02 \cdot 10^{-4}$	No change.
			Electrode covered with a fine crystalline black powder.
−720	−720	$1.7 \cdot 10^{-3}$	Dark gray corrosion products firmly fixed to the electrode surface.
−800	−800		Black readily removable film on the electrode; the surface under this corroded.

This colloidal solution is formed by the hydrolysis of $Fe(NO_3)_3$ and contains positive micelles $Fe(OH)_3Fe^{3+}$, which can be discharged at the cathode.

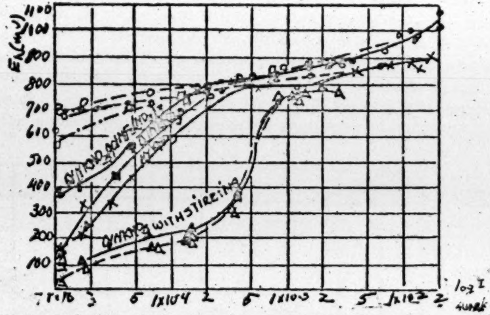


Fig. 1. Cathodic polarization of iron in 0.1 N KNO_3: with stirring (▲ − outward path, △ − return path); in a still solution (■ − outward path, □ − return path); and in a still solution with addition of $Fe(NO_3)_3$ (● − outward path, O − return path)

The absence that we have found of any great effect due to iron ions on the cathodic polarization of iron in 0.1 N KNO_3 is in sharp contrast with the effect of Fe^{3+} ions, as observed by Tomashov [1] in the solution 0.5 N NaCl + 0.005 N Na_2CO_3 + 0.005 N $NaHCO_3$. The cathodic curve for iron, investigated by Tomashov in this solution with additions of $FeCl_3$, reveals an almost complete absence of polarization, resulting from depolarization according to the reaction: $Fe^{3+} + e \longrightarrow Fe^{2+}$; as the concentration of this depolarizer (Fe^{3+}) is high in comparison with the concentration of oxygen (0.001 N), depolarization proceeds mainly on account of ferric ions, with corresponding acceleration of the corrosion process. Consequently, in the case studied by Tomashov, the acceleration of corrosion on account of ferric ions has a cathodic mechanism. In our case, the observed acceleration of corrosion under the action of ferric ions is connected not with a cathodic, but with an anodic process, as shown in our previous communication [4].

Results of investigations on the effect of the HNO_3 concentration on the cathodic polarization of iron are presented in Fig.3. In all experiments, the NO_3' concentration was maintained constant at 0.1 N. Solutions having various pH values were prepared by dissolving the corresponding amounts of acid in 0.1 N KNO_3.

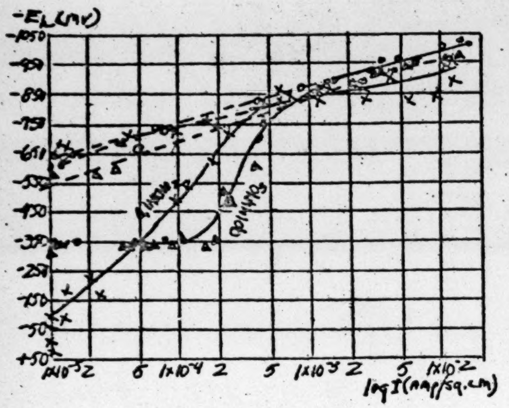


Fig.2. Cathodic polarization of iron: in 0.1 N KNO_3 (X – outward path, x – return path); in 0.01 N HNO_3 (● – outward path, O – return path); in 0.01 N HNO_3 with addition of urea (▲ – outward path, Δ – return path)

A number of interesting relations can be established from the cathodic curves. Increase in the concentration of acid displaces the diffusion threshold in the direction of higher current density. In 0.05 N HNO_3, the polarization was found to be unstable. The return branch of the curve for 0.05 N HNO_3, in contrast with curves for weaker solutions, does not keep to negative values of the potential. In 0.1 N HNO_3, no appreciable polarization is to be observed; at the current densities with which we worked (up to $2 \cdot 10^{-2}$ amp/sq.cm), we did not attain the diffusion threshold. A similar effect of pH on the displacement of the diffusion current was observed by Krasilshchikov [3] when studying the behavior of iron in solutions of sulfuric acid.

The regions of hydrogen evolution for different HNO_3 concentrations do not vary greatly. The return branches of the cathodic curves for solutions of low concentration, right up to 0.01 N HNO_3, do not differ greatly from one another, and in the region of oxygen ionization they pass on the negative side of the outward branches. It is evident that in weakly acid solutions (up to 0.1 N), on switching off the current, the potential is greatly displaced in the negative direction from its original value, because the oxide film is not reformed in these solutions. In 0.05 N HNO_3, the oxide film is reformed when the current density is diminished, and in 0.1 N HNO_3 the film is not removed, even at very high current densities, owing to the powerful oxidizing action of the solution.

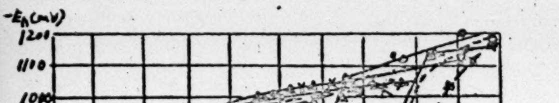


Fig.3. Dependence of the cathodic polarization of iron on the concentration of nitric acid.

We have studied the cathodic polarization of iron also in 0.1 N solutions of $KMnO_4$, $K_2Cr_2O_7$, and $(NH_4)_2S_2O_8$ (Fig.4). The electrode potential of iron is most positive in a solution of potassium permanganate. When working with current densities of the order 10^{-3} amp./sq.cm, we did not attain the diffusion threshold in this solution; the polarization of iron in a $KMnO_4$ solution is not great. After the trials, a compact black film was found on the electrodes, and, on removing it, we obtained fine crystalline MnO_2 powder. The action of $KMnO_4$ as a depolarizer proceeds according to the equation 2; the equilibrium potential of this process is 1.128 V.

The 0.1 N solution of $K_2Cr_2O_7$ that we investigated is employed as a passivator for iron. As Fig.4. shows, iron is very highly polarized in a $K_2Cr_2O_7$ solution, and the return and outward branches of the cathodic curve do not coincide; the final potential is about 300 mV more negative than the initial potential. In the region of hydrogen overvoltage, the curve for 0.1 N $K_2Cr_2O_7$ is disposed rather more in the negative direction than the curve for 0.1 N KNO_3; thus, the potential of iron at a current density of $1\cdot10^{-3}$ amp/sq.cm is respectively −950 mV and −775 mV for these two solutions.

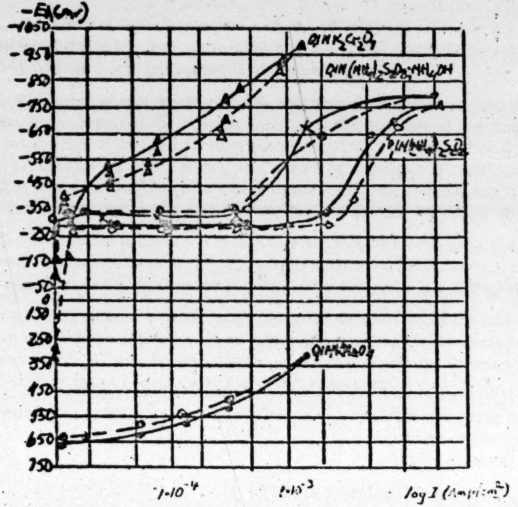


Fig.4. Cathodic polarization of iron in 0.1 N solutions of: $KMnO_4$ (O − outward path, ◐ − return path); $K_2Cr_2O_7$ (▲ − outward path, △ − return path); $(NH_4)_2S_2O_8$ (● − outward path, O − return path); $(NH_4)_2S_2O_8$ with addition of NH_4OH (× − outward path, ◐ − return path)

As was shown in the previous communication [4], the electrode potential of iron in a solution of $(NH_4)_2S_2O_8$, a powerful oxidant, has a fairly high negative value (about −275 mV). The peculiarity of the cathodic curve of iron in this oxidant is the non-polarizability of the electrode up to high values of current density ($1.9\cdot10^{-3}$ amp/sq.cm); the region of hydrogen evolution also is displaced to higher current densities, in comparison with the curves for nitrate solutions. The initial and final potentials of iron after cathodic polarization in $(NH_4)_2S_2O_8$ solution are coincident.

Feeble gas evolution is to be observed already at a current density of $1.37\cdot10^{-5}$ amp/sq.cm, and it becomes more intense at $5.61\cdot10^{-5}$ amp/sq.cm, which corresponds to the beginning of hydrogen evolution. At a current density of $3.43\cdot10^{-5}$ amp/sq.cm, formation of an $Fe(OH)_3$ precipitate is to be observed. It is evident that, owing to fairly intense corrosion, the concentration of Fe^{3+} in the $(NH_4)_2S_2O_8$ solution is so high that separation of hydrogen at the cathode leads to increase in the OH' concentration at the cathode surface until the solubility product of $Fe(OH)_3$ is attained.

At high current densities ($1.94\cdot10^{-2}$ amp/sq.cm) a cloudiness appears in the cathode liquid, caused evidently, by the separation of sulfur in the colloidal condition from the ammonium persulfate. We determined the cathode curve of iron in 0.1 N $(NH_4)_2S_2O_8$ with an addition of NH_4OH (0.1 g-equiv. per liter of solution). In an alkaline medium, the initial potential was somewhat displaced in the negative direction (about 40 mV), and the electrode remained unpolarized up to a current density of $3.4\cdot10^{-4}$ amp/sq.cm, i.e., in this case polarization sets in earlier than in neutral solution. The region of hydrogen evolution begins at a lower current density than for the solution without the NH_4OH addition. Flocs of $Fe(OH)_3$ make their appearance in the cathode space at a lower current density than that at which they appear in a neutral medium; they appear at $1.3\cdot10^{-3}$ amp/sq.cm.

SUMMARY

1. An investigation has been made of the cathodic polarization of iron in nitrate solutions containing nitric acid in varying concentration, the concentration of NO_3' ions being maintained constant. It has been shown that increase in the concentration of acid displaces the diffusion threshold in the direction of higher current density. In 0.1 N HNO_3 the diffusion threshold was not attained for current densities up to $2\cdot10^{-2}$ amp/sq.cm.

In neutral and weakly acid solutions (up to 0.01 N HNO_3), the potential of the iron after the current has been switched off has a greater negative value than the initial potential. For 0.05 N HNO_3, the hysteresis of the cathodic curve is inappreciable because the oxidizing properties of the solution cause an oxide film to be formed rapidly; in the diffusion region, the return curve passes somewhat below the outward curve.

2. The effect of the concentration of KNO_3 on the cathodic polarization of iron has been investigated. It has been found that there is no essential difference between the courses of the cathodic curves in 0.1 N and 1.0 N solutions of KNO_3. It is evident that the main depolarizer in neutral and weakly acid solutions of nitrates is dissolved oxygen, and not NO_3' ions.

3. The effect of ferric ions on the cathodic polarization of iron in 0.1 N KNO_3 has been investigated. It has been found that ferric ions, while displacing the initial electrode potential in the negative direction, produce little change in the further course of the cathodic curve.

4. The effect of urea on the cathodic polarization of iron in an acid nitrate solution has been investigated. In this case, displacement of the diffusion threshold in the direction of lower current density is found. The cathodic polarization of iron in a solution containing KNO_2 (0.1 N) and HNO_3 (0.01 N) was investigated. It was found that in this case the effect of NO_2' ions cannot be explained by their catalytic effect on depolarization by the aid of NO_3' ions. KNO_2 acts as a depolarizer on its own account, and it greatly displaces the initial electrode potential of iron in the positive direction and changes the course of the cathodic curve.

5. The cathodic polarization of iron in 0.1 N solutions of $KMnO_4$, $K_2Cr_2O_7$, and $(NH_4)_2S_2O_8$ has been investigated. It has been found that in $K_2Cr_2O_7$ solution the iron electrode is strongly polarized and, in the hydrogen region, has a higher negative potential than that given in a KNO_3 solution at the same current density.

In a $KMnO_4$ solution over the range of current density studied (up to $6 \cdot 10^{-3}$ amp/sq.cm), the iron electrode is only weakly polarized. In an $(NH_4)_2S_2O_8$ solution, the electrode remains unpolarized up to a current density of $7 \cdot 10^{-3}$ amp/sq.cm; addition of NH_4OH reduces the diffusion threshold in an ammonium persulfate solution to the current density of $5 \cdot 10^{-4}$ amp/sq.cm.

Received November 6, 1951

Laboratory for the Physics of the Metals . .
the All-Union Institute of Aviation Materials
(Order of Lenin)

LITERATURE CITED

[1] N. D. Tomashov. Corrosion of Oxygen-depolarized Metals. USSR Acad. Sci. Press, 1947.

[2] S. Glasstone and A. Hickling, Electrolytic oxidation and reduction, 1935.

[3] A. N. Krasilshchikov. J. Phys. Chem. 20, 1187 (1946).

[4] L. Ya. Gurvich and G. V. Akimov. Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 6, 565 (1950).

MECHANICAL PROPERTIES OF ALLOYS OF THE MAGNESIUM — CADMIUM SYSTEM

E. M. Savitsky and V. V. Baron

The phase diagram for alloys of the magnesium-cadmium system has been studied by many of our own scientists. One of the first was Academician Urazov [1]. This system was investigated by Stepanov and Bulakh [2,3], Kornilov [4,5,6], Ageev and Ageeva [7], Rovinsky and Kozhina [8], Khomyakov, Kholler, and Torshkina [9], and Grum-Grzhimaylo [10]. The system magnesium-cadmium has been studied also by a number of foreign investigators [11,12,13,14,15,16].

As a result, the presence of three compounds: Mg_3Cd, MgCd and $MgCd_3$ has been established in this system. In spite of the large number of investigations, there are a number of obscurities in the structure of the diagram. Some authors consider that, when alloys of the magnesium-cadmium system are crystallized out, the compound MgCd is formed from the melt, and two other compounds, Mg_3Cd and $MgCd_3$, make their appearance in the solid state, when the temperature is lowered, as a result of a disorder → order process.

These authors assert that MgCd undergoes polymorphous change at about 250°. Other authors find that the melts in this system yield only solid solutions, from which, as the temperature is lowered, all three compounds separate as a result of the disorder → order process. According to the results of these investigations, the temperatures of formation of the compounds Mg_3Cd, MgCd, and $MgCd_3$ are 150, 250, and 89° respectively. In the solution of these questions, use may be made of a study of the mechanical properties of the alloys. However, as far as we are aware, the mechanical properties of alloys of the magnesium-cadmium system, apart from hardness determinations at room temperature, have hitherto remained without study. The measurements referred to were carried out only on cast specimens, whereas it is well known that the equilibrium state of alloys is attained appreciably more rapidly and completely when deformed specimens are used [17].

EXPERIMENTAL

In the present work we determined the hardness, tensile strength, plasticity under dynamic and static conditions, and the efflux pressure for cast and deformed alloys of this system in the quenched and annealed conditions at ordinary and at raised temperatures. The alloys were prepared from magnesium of 99.9% purity, mark MG1, and cadmium of 99.8% purity, mark KD 2.

Fusion was carried out under a carnallite flux, and, to prevent burning of the magnesium, the latter was introduced under a layer of melted cadmium. The compositions of the cast alloys are given in the Table.

Hardness measurements were made on cast specimens, 23 mm in diameter and about 50 mm long, at room temperature. The hardness of the alloys was determined with the aid of a Pobedite cone and was calculated from the formula

$$H_{\varepsilon} = \frac{P}{S},$$

where P is the load in kg, and S is the area of the imprint in sq.mm.

The use of a cone instead of a sphere for measurement of the hardness resulted in a similarity between the imprints obtained and permitted the load used in the tests to be varied and the hardness values obtained under various loads to be subsequently compared. The load used for the measurement of hardness at room temperature was 60 kg. After their hardness has been measured, the cast specimens were pressed into rods, 11 mm in diameter. The degree of deformation was 80%, and the average length of the rods was 160 mm. The pressing was carried out in a 35-tonne hydraulic press at 250°. From the rods obtained, specimens were prepared for hardness, plasticity, and tensile measurements.

In order to determine the degree to which the alloys approximated to the equilibrium state and to determine the amount of annealing required for the attainment of equilibrium, various periods of annealing were given — from 2 hrs to 6 days — hardness determinations being made at intervals. We did not detect any characteristic points on the hardness curves for the unannealed alloys in the cast and deformed conditions.

TABLE

Composition of Alloys

Alloy No.	Atom % Cd	Wt. % Cd	Alloy No.	Atom % Cd	Wt. % Cd
1	0	0	16	52	83.3
2	10	33.9	17	54	84.4
3	20	53.6	18	56	85.5
4	23	58	19	58	86.5
5	25	60.6	20	60	87.3
6	26	64.2	21	62	88.3
7	33	69.5	22	67	90.2
8	35	71.3	23	70	91.5
9	39	74.4	24	72	92.2
10	40	75.5	25	73	92.3
11	42	76.9	26	75	93.3
12	44	78.4	27	77.95	94.2
13	46	79.98	28	79.5	94.7
14	48	81.0	29	85.0	96.3
15	50	82.2	30	90	97.6
			31	100	100

After the annealing, and with increase in its duration, minima began to appear on the hardness curves in places that corresponded to the composition of compounds. When deformed specimens of the alloy corresponding in composition to the compound MgCd had been annealed for 4 hrs, the hardness value (70-80 kg/sq.mm) did not change further with further heating at the annealing temperature. However, the hardness of alloys having the compositions of the other two compounds continued to change beyond this period and attained a constant value only after a 4-day annealing; this is to be explained, evidently, by the greater rate at which the compound MgCd attains equilibrium, as compared with the compounds Mg_3Cd and $MgCd_3$. In the process of bringing the alloys to equilibrium by annealing, there is an increase in hardness, due to an aging effect, of alloys having compositions approximating to the compounds Mg_3Cd and MgCd. The hardness curves determined at room temperature for alloys that have been annealed for 6 days show minima for compositions corresponding to each of the three compounds indicated, and they show the least scatter in the hardness values (see Fig.1, curve a).

On the basis of the results of these determinations, and also of those of previous investigations into the rates of change in the solid solutions of the given system [4,5,6,7], all the alloys were annealed for a period of 6 days; for 3 days annealing was carried out at 280° for the purpose of homogenization, and about a day was then given at a temperature somewhat (10-15°) less than the temperature of formation of each of the compounds. In choosing 280° as the homogenization temperature, we took into consideration the fact that the temperature must be high enough for all the alloys to pass into the solid solution region, but not so high as to cause appreciable evaporation in the most readily fusible alloys of the system. All the alloys were sealed for annealing in evacuated glass tubes. Annealing was carried out in a muffle furnace. The temperature was regulated by the aid of a potentiometer. Apart from the hardness measurements already mentioned, measurements of tensile strength and of plasticity under static and dynamic conditions were carried out at room temperature on the alloys that had been annealed for six days according to the procedure given above. The tensile tests were done on Gagarin's machine with autographic recorder, and the plasticity tests were done on a hydraulic press (static) and on a vertical impact tester (dynamic). The load used in the tests was kept constant, being 7 tonne in the static test, while the available work in the dynamic test was 8 kg.m (weight of striker 20 kg, fall 0.4 m). Thus in the compression tests the specimens were not taken to the destruction point; the specimens were of diameter 11 mm and of height 10 mm.

The tensile strength (kg/sq.mm) of the alloys was determined from the usual formula

$$\sigma_B = \frac{P}{F},$$

where P is the maximum load in kg, and F the cross-sectional area in mm just before break. The plasticity of the alloys was determined by the change in the height of the specimens (degree of settling) and was calculated from the formula:

$$\epsilon = \frac{h_0 - h_1}{h_0} \cdot 100\%,$$

where h_0 is the height of the specimen before the test (mm), and h_1 is the height of the specimen after the test (mm).

It will be seen from the results given that annealed alloys having the composition of chemical compounds are distinguished at room temperature by their low hardness and strength (Fig.1, curves a and b) compared with the other alloys of this system. It is curious that, when alloys approximating to compounds in composition are tested for behavior under compression, they show an enhanced plasticity (Fig.1, curves c and d). The maxima for hardness and strength and the minima for plasticity that are to be observed on the curves for these properties evidently correspond to the limits for solid solutions on the basis of the compounds Mg_3Cd, MgCd and $MgCd_3$. The extent of the regions of these solid solutions is best defined by the results on the tensile strength of the alloys. It should be noted that in the present instance the solid solution regions are continguous, and, from the measurements of the mechanical properties, we were unable to detect the presence of transitional heterogeneous regions when passing, by changing the concentrations of the components, from one solid solution to another.

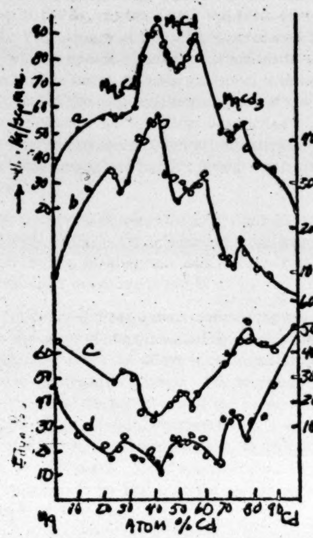


Fig. 1. Mechanical properties of alloys that have been annealed for 6 days: a) hardness; b) tensile strength; c) plasticity under static pressing; d) plasticity under dynamic pressing.

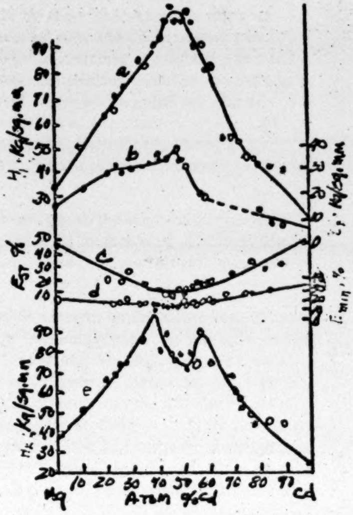


Fig. 2. Mechanical properties of quenched alloys: a) hardness of alloys quenched from 280°; b) tensile strength of alloys quenched from 280°; c) plasticity (static settling) of alloys quenched from 280°; d) plasticity (dynamic settling) of alloys quenched from 280°; e) hardness of alloys quenched from 200°

In order to determine the mechanical properties of the alloys of this system in the solid solution region, we carried out a quenching treatment from 280° with the object of fixing the solid-solution structure in the alloys. The quenching temperature was chosen in the same way as in the case of annealing — it must be sufficiently high for all the alloys to move into the solid solution region, but not too high, because of the tendency of the alloy components to evaporate. The alloys to be quenched were sealed in evacuated tubes and maintained at the quenching temperature for a day. The specimens were then quenched in water. On the specimens heat-treated in this way, measurements were made at room temperature of the mechanical properties that were determined before on annealed alloys. In order to avoid the possibility of the breakdown of the solid solution at room temperature, all the tests were carried out as soon as possible after the quenching treatment. Quenching was therefore done in small batches at a time; in the case of tensile tests, the quenching treatments on the specimens were carried out in succession. Hardness measurements were made not only on specimens quenched from 280°, but also on specimens quenched from 200°. The temperature for the formation of the compound MgCd is disputable, but the presence of this compound at 200° has been confirmed by all investigators of this system. The results obtained by tests at room temperature on specimens quenched from 280° and from 200° are given in Fig.2, and it will be seen that there are no maxima or minima, indicative of chemical compound formation, to be observed on any of the curves for the mechanical properties of alloys quenched from 280°. The courses of the curves are typical for solid solutions.

The hardness and strength of the quenched alloys rise as the percentage content of either component rises from zero, and they attain maxima at about 46 atom % Cd. It should be noted that alloys having compositions corresponding to compounds have higher hardness and strength, and lower plasticity, than the corresponding annealed alloys. For example, the alloy containing 50 atom % Cd (the compound MgCd) had a hardness after quenching of 100 kg/sq.mm, which was reduced to 75-80 kg/sq.mm, i.e. by about 25%, when the alloy was annealed. The strength of this alloy was reduced by the annealing process by 45%, and the plasticity rose by 60-70%. When hardness measurements are made on alloys which have been maintained at 200° for a day and then quenched in water, a single minimum is to be observed at the point corresponding to the compound MgCd. Measurements of the mechanical properties of the annealed and quenched alloys were carried out also at raised temperatures. All the alloys were tested for hardness at 280°, and alloys of composition approximating to MgCd were tested also at 350°; all the alloys were tested for plasticity under dynamic conditions at 280°, and the tensile strength and efflux pressure were determined; also at 280°, for alloys approximating in composition to MgCd.

In the testing of annealed alloys at high temperature, they were brought to the required temperature and held there while on the machines for one hour; they were then tested by the method used at normal temperature. A protective medium was used in tests at 350°. The results of measurements of mechanical properties at high temperature are given in Fig.3.

The courses of the curves representing hardness and plasticity measurements on the alloys at 280° have the same character as the courses of the curves for alloys quenched from this temperature. As was to be expected, at 280° the hardness of the alloys is considerably less, and their plasticity considerably higher, than at room temperature for quenched alloys. The identical qualitative character of the curves representing the properties of alloys quenched from 280° and of the curves for measurements at 280° indicates that the disorder → order process that occurs when the temperature is lowered in alloys of this system proceeds comparatively slowly, and hence it is possible, in the present case, to make use of the quenching method and then measure the properties at ordinary temperature. When measurements are made of hardness at 350°, and of strength and efflux pressure at 280°, on alloys in the region of the compound MgCd, no special points (minima) corresponding to this compound are to be observed.

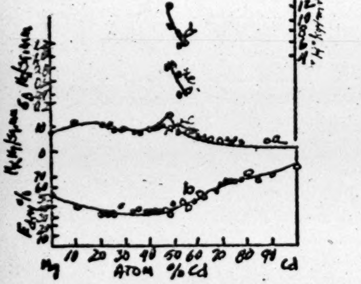


Fig.3. Mechanical properties of alloys at high temperature: a) hardness at 280°; b) plasticity (dynamic settling) at 280°; c) hardness at 350°; d) efflux pressure at 280°; e) tensile strength at 280°.

Investigation of the microstructure of the alloys confirmed the results of the mechanical tests. Thus, alloys corresponding in chemical composition to the compound MgCd which have been quenched from 280° (Fig.4, a)* have the homogeneous structure of a solid solution. When this alloy has been annealed, slippage twinning occurs on the grains of the solid solution owing to the conversion of the solid solution into a chemical compound (Fig.4, b)*; this shows that the compound is formed below 280°.

SUMMARY

1. Mechanical properties of alloys of the magnesium-cadmium system in the annealed and quenched conditions have been measured at ordinary and at high temperatures for the first time.

2. By the method of mechanical tests on annealed alloys, it has been confirmed that the compounds Mg_3Cd, MgCd and $MgCd_3$ are present in the magnesium-cadmium system at room temperature.

3. The curves for the mechanical properties at 280 and 350°, and also the curves for alloys quenched from these temperatures, give no indication of the presence of the compound MgCd. It has therefore been shown that the compound MgCd is formed not from the melt, but from the solid solution, i.e., it is a typical Kurnakov compound.

4. The compounds Mg_3Cd, MgCd and $MgCd_3$ form considerable solid-solution regions and are distinguished

---

* See Plate, page 457-a.

by their high plasticity and low hardness, compared with the solid solutions from which they are formed.

Received October 23, 1951

N. S. Kurnakov Institute of General and
Inorganic Chemistry
Academy of Sciences of the USSR

LITERATURE CITED

[1] G. G. Urazov. Bull. St. Petersburg Polytech. Inst. 14, 675 (1910).

[2] N. I. Stepanov. Proc. Acad. Sci. USSR, 4 (9), No. 3, 72 (1935).

[3] N. I. Stepanov and S. A. Bulakh. Proc Acad. Sci. USSR, 4 (9), No. 31/72, 139 (1935).

[4] I. I. Kornilov. Rate of changes occurring in the solid solutions of magnesium-cadmium alloys, Bull. Acad. Sci. USSR, 1935.

[5] I. I. Kornilov. Bull. Acad. Sci. USSR., Div. Chem. Sci., No. 2, 313 (1937).

[6] N. I. Stepanov and I. I. Kornilov. Bull. Sect. Phys. chem. Anal., 10, 67 (1938).

[7] N. V. Ageev and D. L. Ageeva. Bull. Acad. Sci. USSR, Div. Chem. Sci., No.2, 143 (1946).

[8] V. M. Rovinsky and N. K. Kozhina. X-ray investigation of magnesium-cadmium alloys. United Sci.-Tech. Press, Ministry Heavy Ind. USSR, 1938, No. 38, Trans. All-Union Research Inst. Aviation Mat.

[9] K. G. Komyakov, V. A. Kholler, and V. A. Troshkina. Bull. Moscow State Univ., 6 (1950).

[10] N. V. Grum-Grzhimaylo. Bull. Sect. Phys.-chem. Anal., 19 (1949).

[11] G. Grube, Z. anorg. Chem. 72, (1906).

[12] J. Valentin, Rev. de Metal 23, 209 (1926).

[13] W. Hume-Rothery and S. W. Rowell, J. Inst. of Met., London, 5, 38 (1927), pp. 137-154.

[14] G. Natta, Am. Chem. Appl. 5, 18 (1926), pp. 135-138.

[15] G. Grube and Schiedt, Z. anorg. allg. Chem. 194 (1930).

[16] W. Hume-Rothery and G. Raynord, Proc. of the Royal Soc., ser. of math. and phys. Scien. No.959, 1940, pp. 471-486.

[17] E. M. Savitsky and V. V. Baron. Phase diagram and mechanical properties of alloys of the system Mg-Zn. Proc Acad. Sci. USSR, 14, 3 (1949).

BLANK
PAGE

COORDINATION NUMBERS AND HYDRATION OF THE IONS Li^+, Na^+, K^+, Cl^-, Br^-, AND I^- IN AQUEOUS SOLUTIONS

O. Ya. Samoilov

It has been shown previously [1] that every water molecule in a solution of acid may on the average be represented as $H_{2+\frac{\epsilon}{e}}O^{\frac{\epsilon}{e}+}$, where $\underline{e}$ is the electronic charge and ϵ is a small positive charge associated with the presence in the water molecules of an excess proton. In this connection, measurement of the heats of solution of salts in acids, e.g. HCl, permits an evaluation of the coordination numbers of ions in aqueous solutions, i.e. the average numbers of water molecules that comprise the immediate surroundings of the ions in solution.

We have measured the heats of solution at 25° in aqueous solutions of HCl of various concentrations of the following salts: LiCl, NaCl, KCl, $NaBr \cdot 2H_2O$, $NaI \cdot 2H_2O$ and $N(CH_3)_4Br$. The measurements were carried out in a calorimeter having an isothermal jacket. The procedure used has been described previously [2]. The amounts of the salts taken for solution were such as to yield solutions containing about 0.05 mole of salt per 50 moles of water (in the case of NaCl − 0.17), i.e. so that the concentration was sufficiently small. For each salt, the final concentration of the solution was the same in all experiments.

The dehydration of lithium chloride (chem.pure, recryst.) was carried out by heating it in admixture with chem. pure ammonium chloride (to prevent hydrolysis) and then calcining to remove NH_4Cl completely. The hydrates $NaBr \cdot 2H_2O$ and $NaI \cdot 2H_2O$ were obtained by maintaining the salts (chem.pure, the sodium bromide was recrystallized) in a desiccator at room temperature (15-20°) over 44 and 59% sulfuric acid respectively until constant weight was attained.

The results obtained are given in Table 1. In this table the heats of solution in water of LiCl, NaCl and KCl according to the data of Lange [3] are given also (the figures are interpolated from Lange's data to the salt concentrations employed by us). In Figs. 1 and 2 the relation between the heats of solution and the concentration of HCl in the solvent is shown. The curves are displaced along the ordinate axis, the same scale being retained for all the curves. The heats of solution L are given in kcal per mole of salt dissolving. The concentration of HCl (m) is expressed in moles HCl per 50 moles of water. Individual determinations of $\underline{L}$ are accurate within about 1%.

The heats of solution of the hydrates $NaBr \cdot 2H_2O$ and $NaI \cdot 2H_2O$ were measured, but the slopes of the curves obtained were precisely equal to the slopes of the curves for the anhydrous salts: the difference in heat of solution between the anhydrous salt and the hydrate for a given final salt concentration is constant and equal to the heat of hydration of the anhydrous salt. By the interpolation of the data of Wüst and Lange [3] for anhydrous NaBr and NaI to the concentration that we used, it is possible, with the aid of the determined heats of solution of $NaBr \cdot 2H_2O$ and $NaI \cdot 2H_2O$ in water, to determine the heats of hydration of anhydrous NaBr and NaI to the dihydrates. They are 4.64 and 5.95 kcal/mole respectively. It is known that the heat of hydration in aqueous solution is higher for Br^- than for I^-. The fact that the heat of hydration of the anhydrous salt to the dihydrate is lower for NaBr than for NaI emphasizes the impossibility of comparing heats of hydration of ions in the solid phase and in solution.

The curves obtained have a very low curvature, and the effect of HCl on the heats of solution of the salts may be characterized by the slopes $\Delta L/\Delta m$ of certain "averaged" straight lines. In so doing, the choice of units for the expression of the concentration is more or less arbitrary: the only thing that is essential for our further considerations is that weight units should be used. In Table 2 the values of β are given for the investigated salts $\left(\beta = -\frac{\Delta L}{\Delta m}\right)$. $\frac{\Delta L}{\Delta m}$ as found from the experimental data by the method of least squares. The values of β are expressed in cal/mole per unit change in m.

With increase in the concentration of HCl in the solution in which dissolution of the salts under investigation is proceeding, there is an increase both in the concentration of H^+ ions, which corresponds to an increase in

TABLE 1

Integral Heats of Solution of Salts in Aqueous Solutions of HCl at 25°C

Salt Dissolved	Conc. of HCl(mole/50 mole H_2O)	Heat of Solution (kcal per mole salt)
LiCl	0.00	+8.69
	0.00	+8.74•
	0.50	+8.39
	1.26	+8.14
	1.26	+8.05
	1.80	+7.84
	2.58	+7.50
	2.58	+7.50
NaCl	0.00	−1.02
	0.00	−1.03•
	0.32	−1.14
	0.32	−1.14
	0.76	−1.23
	0.76	−1.24
	1.14	−1.30
	1.14	−1.29
	1.72	−1.41
	2.78	−1.64
$NaBr{:}2H_2O$	0.00	−4.64
	0.40	−4.76
$NaBr{:}2H_2O$	0.83	−4.79
	1.69	−4.90
	3.50	−5.16
$NaI \cdot 2H_2O$	0.00	−4.25
	0.83	−4.34
	1.68	−4.36
	2.37	−4.46
	3.47	−4.57
KCl	0.00	−4.24
	0.00	−4.26•
	0.32	−4.31
	0.33	−4.31
	0.61	−4.31
	0.77	−4.32
	1.14	−4.34
	1.72	−4.31
	2.70	−4.34
$N(CH_3)_4Br$	0.00	−5.44
	0.81	−5.01
	1.64	−4.72

• According to Lange's data.

the positive charge of each molecule of water (of the ions $H_{2+\frac{\epsilon}{e}}O^{\frac{\epsilon}{e}+}$) in the solution [1], and also in the concentration of Cl^- ions. However, owing to the special nature of the hydrogen ion in aqueous solutions, only the increase in the concentration of H^+ ions has any effect on the heats of solution of the salts.

In actual fact, the interaction with ions of the dissolved salts of the greater part of the positive charges of the $H_{2+\frac{\epsilon}{e}}O^{\frac{\epsilon}{e}+}$ ions is compensated by the negative charges of the Cl^- ions, for the solution as a whole is electrically neutral. However, the immediate surroundings of the hydratable cations (e.g. Li^+, Na^+) are composed mainly of water molecules. The same can be said of the surroundings of the anions (e.g. Cl^- for the dissolution of LiCl or NaCl). It will be assumed henceforth that the immediate surroundings of ions in aqueous solutions are always composed of water molecules only (which is in any case correct in dilute solution). In the first co-ordination layer of the ions, accordingly, only the positive charges of these molecules are present. A corresponding number of negative charges (Cl^- ions) are distributed outside the first coordination layer, but they have no effect on the heat of solution. The point is that the energy of their interaction with ions depends to an insignificant effect on the ionic radius. It may be assumed that it depends only on the ionic charge•, and interaction with cations of the dissolved salts is compensated by interaction with anions. Thus, the heat of solution of salts changes with increase in the concentration of acid in the solvent only as a result of the influence of increase in the effective positive charge of the water molecules that comprise the immediate surroundings of the dissolved ions. The slopes of the heat of solution curves are determined by the difference between the energies of interaction with cations and with anions. As these energies depend on the average numbers of water molecules comprising the immediate surroundings of ions, i.e. the coordination numbers of ions in solution, the possibility of the evaluation of these numbers emerges.

The energy of Coulomb interaction of the positive charges of the ions $H_{2+\frac{\epsilon}{e}}O^{\frac{\epsilon}{e}+}$ in a solution of acid with cations and anions having unit charge may be written respectively:

$$E_c = -\frac{n_c \cdot e \cdot \epsilon}{R_c} \qquad \text{and } E_a = \frac{n_a \cdot e \cdot \epsilon}{R_a},$$

• Dependence on the radius is to be found only when the radius determines the distance between the particles. In liquids, where there is a rapid diminution in orderliness in the relative disposition of particles as the distance between them increases, the distribution of particles that are sufficiently far removed from one another is practically independent of their radii. The assumption that this dependence ceases to have effect already beyond the limits of the first coordination layer is, of course, a well known simplification.

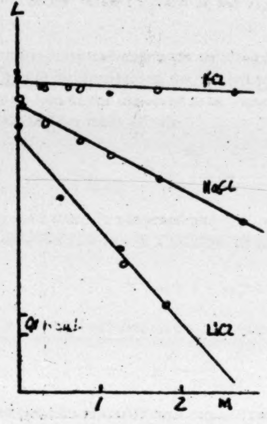


Fig. 1. Integral heats of solution of LiCl, NaCl and KCl in aqueous solutions of HCl: O – according to the results of the present work; ● – according to Lange's results.

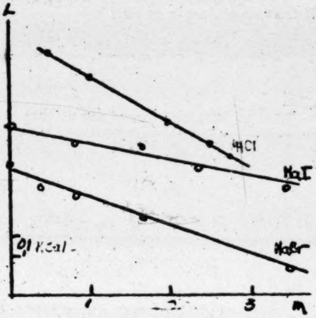


Fig. 2. Integral heats of solution of NaBr·2H_2O and NaI·2H_2O in aqueous solutions of HCl, and differential heats of solution of HCl: O – according to the results of the present work; ● – according to data in reference tables.

TABLE 2

Values of β for the salts investigated

Salt	LiCl	NaCl	NaBr	NaI	KCl
β	465	210	142	91	11

where n_c and n_a are the coordination numbers of the cation and anion in solution, e is the electronic charge, ϵ is the mean positive charge of the water molecules of the ions $\left(H_{2+\frac{\epsilon}{e}}O^{\frac{\epsilon}{e}+}\right)$ in a solution of acid (here one should speak of the effective value of ϵ), and R_c and R_a are the distances of the charge of the water molecules in the first coordination zones of the ions to the centers of the ions. The minus sign corresponds here to the repulsion of the positive charges from the cations of the dissolved salts (i.e. to a diminution in the exothermicity of the dissolution process).

We shall assume that the charge ϵ is related to the HCl concentration according to the equation ϵ = km (this, of course, follows from the model on which we have based all these considerations). As regards the coefficient k, it has in any case a constant value for low HCl concentrations, and, in this connection, the slopes of the L – m curves should be compared for different salts at a given HCl concentration. However, the experimental results (an almost linear relation between L and m) indicate that the proportionality holds over a wide range of HCl concentrations. It is therefore permissible to compare the mean slopes of the curves ($\Delta L/\Delta m$). R_c and R_a are not known, owing to a certain indefiniteness in the position of the charge ϵ inside the water molecule and also of the orientation of the $H_{2+\frac{\epsilon}{e}}O^{\frac{\epsilon}{e}+}$ ion with respect to the ions of the dissolved salts.

It is natural to equate R_c and R_a to $r_c + r_{H_2O}$ and $r_a + r_{H_2O}$, respectively, where r_c and r_a are the crystallographic ionic radii, and r_{H_2O} = 1.38 A, the radius of a water molecule. This, of course, amounts to an averaging-out of the position of the charge ϵ. It is not likely that this averaging process will lead to appreciable error: of the two orientations that can be assumed for the ion $H_{2+\frac{\epsilon}{e}}O^{\frac{\epsilon}{e}+}$ with respect to the ions of the dissolved salts, one corresponds to a value of R somewhat lower, and the other to a value somewhat higher, than $r + r_{H_2O}$.

Thus,

$$E_c = -\frac{n_c\cdot e\cdot k\cdot m}{r_c + 1.38}\cdot 10^8 \quad \text{and} \quad E_a = \frac{n_a\cdot e\cdot k\cdot m}{r_a + 1.38}\cdot 10^8 \qquad (1)$$

The factor 10^8 arises because E_c and E_a are expressed in ergs, while the radii of the ions and of water molecules are given in A.

By multiplying expression (1) by Avogadro's number $\underline{\underline{N}}$ and by the erg-calorie conversion factor $(0.2389 \cdot 10^{-7})$, and by introducing the symbol $\underline{K}$ for $2.389\ \underline{Nek}$, we obtain the energy associated with the interaction between ions of the dissolved salts and the positive charges of water molecules in acid solutions expressed in calories per mole of salt:

$$E = -K \frac{n_c}{r_c + 1.38} - \frac{n_a}{r_a + 1.38} \cdot m, \; K > 0.$$

In accord with the proposed interpretation of the effect of hydrogen ions on the heats of solution of salts, the heat of solution of a salt in a solution of HCl of concentration $\underline{m}$ is

$$L = L_0 + E = L_0 - K\left(\frac{n_c}{r_c + 1.38} - \frac{n_a}{r_a + 1.38}\right) \cdot m,$$

where L_0 is the heat of solution of the salt in water. Thus,

$$K\left(\frac{n_c}{r_c + 1.38} - \frac{n_a}{r_a + 1.38}\right) = \beta. \qquad (2)$$

Writing down the difference of such expressions (2) for two salts having identical anions, but different cations, we obtain

$$K\left(\frac{n_{c_1}}{r_{c_1} + 1.38} - \frac{n_{c_2}}{r_{c_2} + 1.38}\right) = \beta_1 - \beta_2. \qquad (3)$$

The expressions (2) and (3) make it possible to evaluate the quantities n_c and n_a. However, there is still the relation between the coordination number of the ions and their hydration to consider.

Coordination numbers cannot be used directly for the characterization of the hydration of the individual ions, since the sizes of the ions would not then be taken into account. In order to characterize the hydration it is necessary to examine the closeness of the distribution of water molecules around the ions. As a measure of hydration we may take the value of the surface density of distribution of water molecules in the first coordination layer of the ions,

$$\rho' = \frac{n}{4\pi(r + 1.38)^2}, \; ^{*}$$

where $\underline{n}$ is the coordination number of the ion, $\underline{r}$ is its radius, and $4\pi(r + 1.38)^2$ is the area of the first coordination sphere in $\mathring{A}^2$. The value of ρ' for the individual ions may be compared with the corresponding value for water molecules in water:

$$\rho'_{H_2O} = \frac{n_{H_2O}}{4\pi R^2},$$

where n_{H_2O} is the mean coordination number of water molecules in water, and $\underline{R}$ is the mean distance between the centers of adjacent molecules in water. At 25° n_{H_2O} and $\underline{R}$ have the values, respectively, of 4.6 and 2.90 Å [4]**; $\rho'_{H_2O} = 0.044\ \mathring{A}^{-2}$.

It is expedient to characterize the hydration of ions by the density of the distribution of water molecules around them because the phenomenon of hydration in aqueous solutions manifests itself in the influence of the ion on the translatory motion of water molecules (principally the nearest water molecules). As we have previously shown [5], the density of distribution of particles in a liquid is related to their translatory movements. Increase in translatory motion corresponds to increase in the number of local rarefications in the liquid and therefore to a diminution in density; diminution in the translatory motion corresponds to an increase in density.

---

* The prime is used to distinguish from the well known radial distribution function $\rho(r)$, which corresponds to a volume density.

** The radius of the first coordination sphere must here be definitely considered as equal to the mean distance between the centers of adjacent molecules in water, which has been measured with adequate accuracy by Morgan and Warren [4]. The crystallographic radii for the ions and water molecules are used owing to the absence of reliable measurements of the mean distances between the centers of the ions and the centers of the water molecules that are closest to them in aqueous solutions.

It has been shown that ions that undergo hydration increase the activation energy for the viscous flow of the neighboring water molecules, i.e. diminish their translatory motion [6,7] and hence for such ions

$$\rho' > \rho'_{H_2O} \tag{4}$$

On the other hand, a number of ions (K^+, Cl^-, Br^-, I^-) increase the translatory motion of the neighboring water molecules (this case has been called negative hydration [7]). For such ions the following inequality must hold*:

$$\rho' < \rho'_{H_2O}. \tag{5}$$

The inequalities (4) and (5) permit an evaluation of the lower limits of the coordination numbers of the ions that are hydrated and of the upper limits of the coordination numbers of the non-hydrating ions (negative hydration). Thus, $n_{Na^+} > 3.05$; $n_{K^+} < 4.02$; $n_{Cl^-} < 5.57$.

From a comparison of the values of β for NaCl and NaBr ($NaBr \cdot 2H_2O$), it is possible to indicate the lower limit of the value of K in the relations (2) and (3). Subtracting the expression (2) for NaBr from the corresponding expression for NaCl, we obtain:

$$K\left(\frac{n_{Br^-}}{3.34} - \frac{n_{Cl^-}}{3.19}\right) = 68, \tag{6}$$

from which it will be seen that $n_{Br^-} > n_{Cl^-}$, since $K > 0$. On the other hand, a comparison of the heats of hydration of the ions Cl^-, Br^-, and I^-, and also of a number of properties of chloride, bromide, and iodide solutions, leads to the view that in this series the negative hydration of the ions increases. The inequality $\rho_{Br^-} < \rho_{Cl^-}$ must therefore hold, from which it follows that $n_{Br^-} < 1.096\, n_{Cl^-}$. Substituting this limiting n_{Br^-} in formula (6), we obtain $0.0147\, K \cdot n_{Cl^-} > 68$ or

$$K > \frac{68}{0.0147\, n_{Cl^-}}. \tag{7}$$

We obtain the lower limit of K by substituting in formula (7) the upper limit of n_{Cl^-}. From the expression (2) for KCl it will be seen that $\frac{n_{K^+}}{2.71}\ \frac{n_{Cl^-}}{3.19} > 0$, and since $n_{K^+} < 4.02$, therefore $n_{Cl^-} < 4.74$ (this figure is less than that given by the equation $\rho'_{Cl^-} < \rho'_{H_2O}$). Correspondingly $K > 976$.

We are now in a position to indicate the lower limit of n_{K^+}. From expression (3) for NaCl and KCl:

$$n_{K^+} = 2.71\left(\frac{n_{Na^+}}{2.36} - \frac{199}{K}\right),$$

from which it follows that $n_{K^+} > 2.95$, since $n_{Na^+} > 3.05$ and $K > 976$. From the expression (2) for LiCl it is possible to determine the upper limit of the coordination number of the lithium ion; it is 4.23.

If we make use of the slope of the curve for the dependence of the differential heats of solution of HCl on its concentration, the limits of possible values of n_{K^+} can be narrowed, and the value of K can be evaluated. The curve $-\Delta H$, m for HCl, constructed from tabulated data [8], is given in Fig.2 (ΔH, it is true, refers to 18°). The value of $\beta = \Delta H/\Delta m$, calculated by the method of least squares, is 233 cal/mole per unit change in m.

The difference between the heat content of a mole of HCl in infinitely dilute solution and in a solution of concentration m is associated with the interaction of $H_{2+\frac{\epsilon}{e}}O^{\frac{\epsilon}{e}+}$ ions in the solution with chloride ions, and also among themselves. It is not difficult to see that for low m the following equation, analogous to (2), is approximately obeyed for the curve constructed:

$$K\left(\frac{n_{H^+}}{R} - \frac{n_{Cl^-}}{3.19}\right) = 233, \tag{8}$$

where n_{H^+} is the coordination number of water molecules $\left(H_{2+\frac{\epsilon}{e}}O^{\frac{\epsilon}{e}+}\text{ ions}\right)$ that do not enter into the immediate surroundings of the Cl^- ions. n_{H^+} must be taken as equal to the coordination number of water molecules in water (4.6 at 25°); R has the value 2.90 A (the mean distance between neighboring molecules in water according to the radial distribution curve) [4].

---

* The peculiarities of water [5] are here of no significance since the distribution of the molecules around the ions is under consideration.

Subtracting equation (2) from (8), we obtain for KCl:

$$K\left(\frac{4.6}{2.90} - \frac{n_{K^+}}{2.71}\right) = 222, \qquad (9)$$

from which it follows that $n_{K^+} > 3.68$, since $K > 976$. Thus for n_{K^+} we have $3.68 \leq n_{K^+} \geq 4.02$. We will take n_{K^+} as equal to $\frac{3.68 + 4.02}{2} = 3.8$. Substituting this value of n_{K^+} in equation (9) we obtain $K = 1.17 \cdot 10^3$.

By evaluating K in this way from the determined experimental values of β by the aid of equations (2) and (3), we shall find the coordination numbers of the ions Li^+, Na^+, Cl^-, Br^-, I^-. The coordination numbers (n) and also ρ' for these ions are given in Table 3.

The values of n found are close to the mean coordination number of water molecules in water, which points to the determining significance of the structure of water for the structure of dilute ionic solutions. In this sense, the results of the present work do not differ essentially from the conclusions of Bernal and Fowler [9], who, on the basis of a calculation of the energy of the coordination by ions of the water molecules of the solution, considered that the coordination number of a singly charged ion in aqueous solution is four.

TABLE 3

n (the Coordination Number in Aqueous Solution) and ρ' for the Ions Li^+, Na^+, K^+, Cl^-, Br^-, I^- at 25°

Ion	Li^+	Na^+	K^+	Cl^-	Br^-	I^-
n	3.8	3.7	3.8	4.4	4.8	5.3
ρ'	0.065	0.053	0.042	0.035	0.034	0.033

In conclusion I express my thanks to A. F. Kapustinsky for his cooperation in the performance of this work.

SUMMARY

1. The integral heats of solution of LiCl, NaCl, KCl, $NaBr \cdot 2H_2O$, $NaI \cdot 2H_2O$ and $N(CH_3)_4Br$ in aqueous solutions of HCl of various concentrations have been measured at 25° in a calorimeter with an isothermal jacket.

2. A thermochemical method for the evaluation of coordination numbers of ions in aqueous solutions has been developed. The coordination numbers of Li^+, Na^+, K^+, Cl^-, Br^-, I^- have been determined at 25°. In dilute solutions they are close to the mean coordination number of the water molecule in water.

3. The following expression is proposed as a measure of the hydration of ions; $\rho' = \frac{n}{4\pi(r + 1.38)^2}$, where n is the coordination number of the ion in solution, r and 1.38 are the radii (in A) of the ion and of the water molecule respectively, ρ' is the surface density of distribution of water molecules in the first coordination layer of the ions. For ions that undergo hydration $\rho' > \rho'_{H_2O}$, and for non-hydrating ions (negative hydration) $\rho' < \rho'_{H_2O}$.

Received November 1, 1951

N.S. Kurnakov Institute of General and
Inorganic Chemistry
USSR Academy of Sciences

LITERATURE CITED

[1] O. Ya. Samoilov. Proc. Acad. Sci. USSR, 81, 641 (1951).

[2] A. F. Kapustinsky and O. Ya. Samoilov. Bull. Acad. Sci. USSR. Div. Chem. Sci. No. 4, 337 (1950).

[3] Landolt-Bornstein, Phys.-Chem. Tabellen, 5. Aufl., I Erg-Bd., 841-842, 1927.

[4] S. Morgan, B. E. Warren, J. Chem. Phys. 6, 666 (1938).

[5] O. Ya. Samoilov, J. Phys. Chem., 20, 1411 (1946).

[6] O. Ya. Samoilov, Bull. Acad. Sci. USSR, Div. Chem, Sci. No. 1, 30 (1945).

[7] O. Ya. Samoilov, Proc. Acad. Sci. USSR, 77, 633 (1951)..

[8] E. V. Britsky, A. F. Kapustinsky and co-workers. Thermal Constants of Inorganic Substances. Acad. Sci. USSR Press, 1949.

[9] D. Bernal and R. Fowler. Prog. Phys. Sci., 14, 586 (1934).

THE NATURAL SORBENTS OF THE FAR EAST

COMMUNICATION 1. ELECTRON-MICROSCOPIC INVESTIGATIONS OF NATURAL SORBENTS

V. T. Bykov, V. M. Lukyanovich, and L. V. Radushkevich

There is a wide distribution in nature of highly dispersed substances having a large internal (specific) surface that is accessible to vapors and liquids and may attain the area of tens or hundreds of square meters per gram of material; these we bring together under the general name of "natural sorbents". Natural sorbents, owing to their ready accessibility and low cost are widely used in industry. In the investigation of the quality of natural sorbents, we meet with the necessity of studying their skeletal structure, the degree of dispersion of the particles, and the structure of these particles.

For the main part, natural sorbents are complex polymineral formations with a varied structure in their component particles and in the nature of the surface of these particles. Adsorption investigations permit us to obtain an idea of the structure of the pores and the size distribution of the pores, and moreover, the application of the electron microscope to the investigation of the skeleton of the natural sorbents permits certain conclusions to be drawn concerning the degree of subdivision of the natural product, of the form of the particles that compose it, and of the character of the macro- and transitional porosity of the natural sorbent. Apart from this, electron-microscopic investigation of natural sorbents permits the observation of the mineralogical varieties composing the given natural sorbent and the estimation of their approximate proportions. Hence in embarking on a general investigation of the sorption properties and structure of natural sorbents, we made use of the electron-microscopic method of investigation.

In conjunction with chemical and thermographic analysis, the electron-microscopic method of investigation permitted, in many cases, the establishment or more precise determination of the mineralogical composition of the natural sorbent. The procedure used in the electron-microscopic investigations was as follows. The adsorbent powder was shaken up with water and allowed to stand, generally for $\frac{1}{2}$ or 1 hr, after which a drop of the suspension was applied to a collodion film, which served as a support. When it had dried, the preparation was examined in the electron microscope, and the most characteristic places were photographed.

Electron-microscopic Investigation of the Main Types of Sorbent

The natural sorbents comprise minerals of various composition and origin and of appreciable or high absorptive power. The following main typical varieties of natural sorbents may be distinguished:

a) ash tuffs and their weathering products;
b) decomposed agglomerate tuffs of old quaternary volcanos;
c) bentonite clays;
d) diatomites.

Ash Tuffs and their Weathering Products. Ash tuffs were formed as a result of the deposition of ash in water and did not later suffer migration, as a rolling tendency is not to be observed even in the detritus masses of psammitic tuff [1]. In their chemical composition, the ash tuffs are very homogeneous and may be considered to be analogs of the trachyliparites. The formation of ash tuff deposits belongs to the pliocene or upper miocene.

Weathering processes have affected ash tuffs in varying degree. In the photographs No. 1 and 2 of samples of ash tuff, particles of volcanic ash, 1-3μ across and with well defined edges, are visible; on these there are only slight signs of the formation of weathering products — hydrate forms of aluminohydrosilicates. In the photographs No. 3 and 4 of samples No. 19 and 17 of ash tuffs, the formation of hydrate forms of high porosity is now more readily visible. The formation of argillaceous minerals by the weathering of volcanic ash tuffs is confirmed also by the results of thermal analysis. The thermogram of sample No. 18 of ash tuff, the electron-microscope picture of which is given in Fig. 1, establishes the formation of halloysite (Fig.5), while for the ash tuff No. 17, which shows a high degree of weathering under the electron microscope (picture No.4), the thermogram (Fig.6) indicates the presence of a mixture of the minerals halloysite and montmorillonite, identified by their characteristic endothermic effects, at 590° for the first, and at 695° for the second.

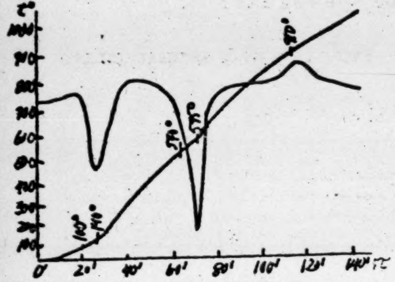


Fig. 5. Thermogram for Sample No.18 of Ash Tuff

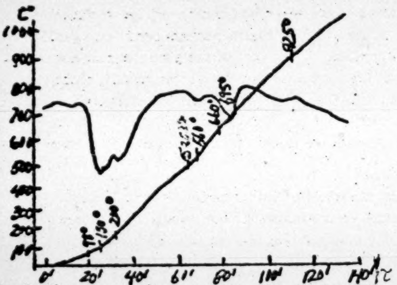


Fig. 6. Thermogram for Sample No. 17 of Ash Tuff

The process of disintegration in particles of volcanic ash is seen particularly clearly in photograph No.7, in which a single grain of volcanic glass has undergone surface disintegration with formation of fissures and translucent plates of argillaceous minerals. In photograph No.8 of a sample of decomposed tuff No. 20, there can be seen large numbers of platelike crystals of montmorillonite and characteristic "curls" of montmorillonite. The formation of montmorillonite and halloysite from volcanic glass in ash tuffs leads to increase in the specific surface of these minerals and to a rise in the limiting sorption values of vapors.

The table shows the results of determinations of the specific surface and of the limiting sorbed volume of benzene, obtained by one of us in a vacuum sorption apparatus [2].

Decomposed Agglomerate Tuffs. Geological investigations have brought to light a number of old-quaternary volcanos, the slag cones of which serve as sources of porous, spongy tuff material [3]. Slag cone material (agglomerate), to an extent that depends on the amount of weathering that occurs under the influence of atmospheric reagents (water and carbon dioxide), undergoes decomposition with formation of aluminohydrosilicates, i.e. clay-like minerals.

In the course of the weathering process, deposits of argillaceous minerals are formed in the pores of the agglomerate; the agglomerate becomes more open in structure, and, as the decomposition process proceeds, a powder is formed, known as decomposed agglomerate tuff. Decomposed agglomerate tuffs are characterized by fairly high adsorption properties (see table). The electron-micrographs Nos 9, 10, 11, 12 of samples of decomposed agglomerate tuffs show the high dispersion of the constituent particles and the conversion of a considerable part of the volcanic glass into the argillaceous mineral montmorillonite. The high degree of dispersion of the particles of the decomposed agglomerate tuff No. 87 is in agreement with the high sorption properties of this tuff, which in its qualities as a sorbent is superior even to activated gumbrin.

Bentonite Clays. It has been possible to establish by means of the electron microscope that samples of these clays are composed of coarsely lamellar montmorillonite (photographs No.13 and 14). Without activation, their absorptive power is not great, but chemical activation leads to a sharp rise in sorptive capacity. In contrast to polymineral formations, such as the decomposed agglomerate tuffs, bentonite clays consist mainly of montmorillonite, as can be seen from a large number of electron-microscope observations that we have made (unfortunately, limitations of space prevent us from showing these photographs).

In some cases the electron microscope permits the ready identification of argillaceous minerals, if they are of the montmorillonite type. For example, in photograph No. 15, which is of a sample of kaolin from Glukhov*, , crystals of kaolinite of pseudohexagonal form are excellently visible, and it can be seen that the whole mass of the clay consists of these crystals. Examples of the determination of the mineralogical composition of clays by means of the electron microscope are given in a paper by Vikulova [4].

---

*The sample of kaolin was presented by M. L Kuadzhe, to whom the authors express their indebtedness.

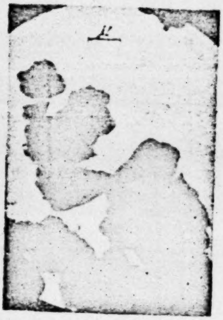


Fig. 1. Ash tuff No. 18 (X 8000).

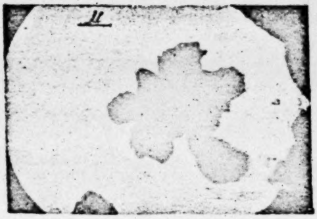


Fig. 2. Ash tuff No. 18 (X 8000).

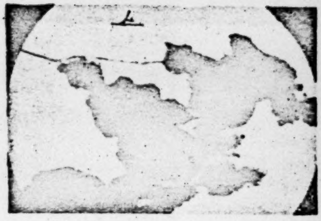


Fig. 3. Ash tuff No . 19 (X 8000).

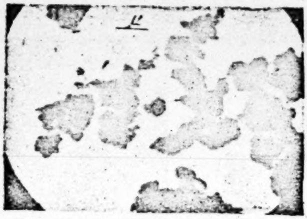


Fig. 4. Ash tuff No. 17 (X 8000).

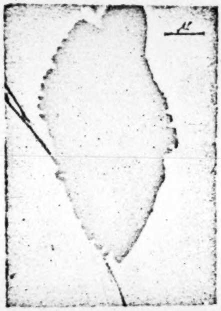


Fig. 7. Grain of volcanic glass from sample of decomposed tuff No. 20 (X 10,600).

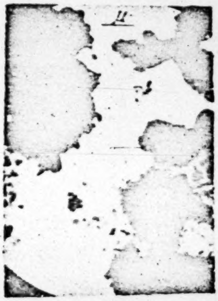


Fig. 8. Sample of decomposed tuff No. 20 (X 8000).

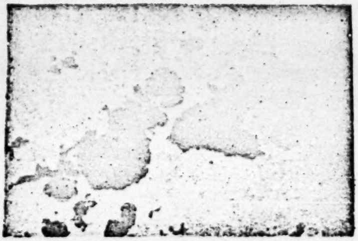


Fig. 9. Decomposed agglomerate tuff No. 88 (X 8000).

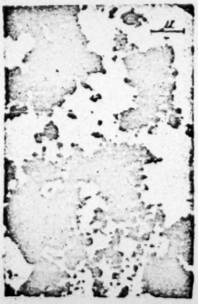


Fig. 10. Decomposed agglomerate tuff No. 87 (X 8000).

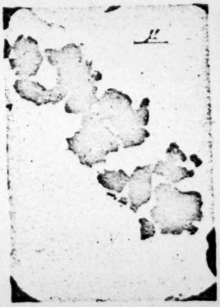


Fig. 11. Decomposed agglomerate tuff No. 95 (X 8000).

Fig. 12. Decomposed agglomerate tuffs No. 173 (X 8000).

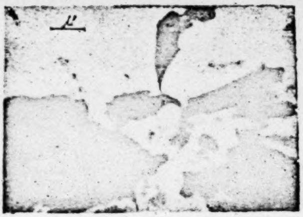


Fig. 13. Sample No. 42, Montmorillonite clays (X 8000).

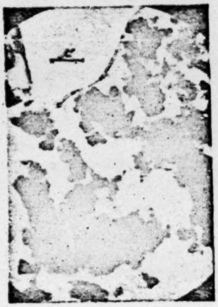


Fig. 14. Sample No. 43, Montmorillonite clays (X 8000).

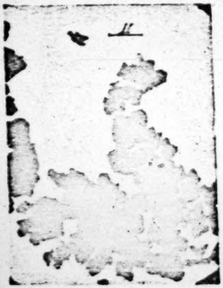


Fig. 15. Sample of kaolin (X 8000).

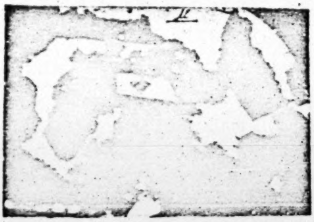


Fig. 16. Diatomaceous sludge from sea bottom, 820 m deep, No. 161 (X 8000).

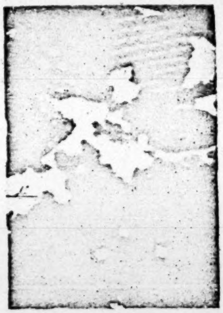


Fig. 17. Diatomaceous sludge from sea bottom, 820 m deep (X 8000).

TABLE

Sorption Properties of Natural Sorbents

Name of samples	Volume of sorbed benzene (cc/g)		Specific surface of the sorbent skeleton S (sq.mm/g)
	at the pt. at which hysteresis begins	at complete saturation	
Ash tuffs No. 18	0.018	0.136	40
" No. 19	0.021	0.087	34
" No.17	0.013	0.141	26
" (decomposed) No.20	0.014	0.164	60
" " No.130	0.017	0.147	55
Decomposed agglomerate tuffs No. 87	0.027	0.369	87
" " " No.88	0.099	0.844	195
" " " No.95	0.031	0.162	57
" " " No.173	0.044	0.290	76
Bentonite clays No. 42	0.025	0.179	40
Kaolin clay No. 77	0.060	0.276	78
Diatomites No. 81	0.019	0.323	26
" No. 142	0.018	0.176	29
Diatomaceous sludges No. 161	0.007	0.133	15
" " No. 162	0.005	0.110	9

Diatomites and Diatomaceous Sludges. The identification of diatomites can be carried out very effectively by means of the electron microscope, the remnants of the siliceous diatom skeletons being readily visible. The diatomites investigated by us (tests No. 81 and 142) also showed the presence of remnants of the siliceous skeletons of diatomaceous algae. When investigating the sorptive properties of diatomites and of modern diatomaceous deposits (sludges), we incidently obtained photographs of diatomaceous sludges*, parts of which are given in Fig. 16 and 17. These are photographs of diatomaceous deposits taken from a depth of 820 m at the bottom of the sea at horizons of 43-45 and 175-178 cm. Such photographs should be of great interest to paleobotanists. A detailed examination in the electron microscope of diatomites and modern diatomaceous deposits indicates the greater opalization of the siliceous skeletons in the diatomites, evidently because of the greater sorptive power of the latter, as compared with diatomaceous sludges (see Table).

SUMMARY

1. Electron-microscopic investigation of natural sorbents has permitted qualitative observations to be made concerning the character of the subdivision of the basic material composing the mineral, has enabled certain quantitative ideas concerning the dimensions of the particles, i.e. the degree of dispersion, to be obtained, and, in conjunction with knowledge of the chemical composition and with the thermal analysis, has, in many cases, indicated the basic mineral formations composing the given natural sorbent. For monomineral material, the mineralogical composition can be very readily determined.

2. Further work must be directed to the development of a procedure for separating polymineral substances into their separate components, which must be compared with standard samples of monomineral substances (kaolinite, halloysite, montmorillonite, etc.) of definite composition and structure in order to give a quantitative idea of the mineralogical composition of the natural sorbent under investigation.

Received November 5, 1951

Institute of Physical Chemistry of the
USSR Academy of Sciences

LITERATURE CITED

[1] E. F. Maleev. Bull. Far-East. Affil. Inst. Acad. Sci. USSR, No. 28 [1], 37 (1938).

[2] V. T. Bykov. Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 6, 678 (1951).

[3] E. F. Maleev, Soviet Geology, No. 12, 45 (1945).

[4] M. F. Vikulova. Soviet Geology No. 39, 121 (1949).

---

* The samples of diatomaceous sludges were obtained by us from P. L. Bezrukov, to whom the authors are very grateful.

BLANK
PAGE

THE EFFECT OF ALTERNATING CURRENT ON THE ELECTRODEPOSITION OF NICKEL

A. T. Vagramyan and A. A. Sutyagina

Alternating current is widely used in the study of various kinds of electrochemical processes, and also for effecting or improving a number of technological processes. Thus, alternating current is used in the study of the structure of the electrical double layer [1], for the elucidation of the kinetics of the formation and dissolution of oxide films [2], in the study of the discharge and ionization of hydrogen [3], and also for the anodic dissolution of various metals (Cr, Mn, Pt, etc.) [4].

Studies have been made in a number of papers of the effect of the superposition of an alternating current on the cathodic process in the electrodeposition of metals. Thus, Izgaryshev, Kudryavtsev, and Berkman [5], Kohlschutter and co-workers [6], and others have noted a considerable reduction in the polarization of the cathode in the electrodeposition of nickel. There are also papers showing that the superposition of an alternating current during the electrodeposition of metals greatly affects the structure of the deposit [6, 7]. In spite of these investigations on this subject, the causes of the change in structure of electrolytic deposits and of the reduction in the degree of polarization of the electrode remain obscure. In the present investigation, some supplementary data concerning the effect of an alternating current on the electrodeposition of nickel are brought forward.

EXPERIMENTAL

In our study of the effect of alternating current on the structure of electrolytic deposits of nickel we used the following circuit (Fig.1); AC is an accumulator, C a condenser, mA d.c. and a.c. milliammeters, R_1 and R_2 rheostats, Dp a choke, E the source of a.c, A the anode, K the cathode, and B an auxiliary nickel electrode for the superposition of the alternating current. Electrodeposition of nickel was carried out from electrolyte of the following composition:

$NiSO_4 \cdot 7H_2O$	250 g/liter
NaCl	5 g/liter
H_3BO_3	30 g/liter
pH	5,4-6

The temperature of the electrolyte was 20°.

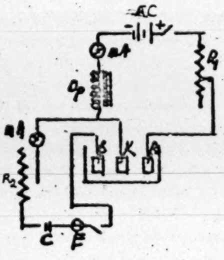


Fig. 1

For the electrodeposition of nickel the density of the direct current was varied from 1 to 3 amp/sq.dm, and the density of the superimposed alternating current was varied also from 1 to 3 amp/sq.dm. The structures of the electrolytic deposits of nickel, as exhibited by the electron microscope "replica" method (magnification 7000), are shown in Figs. 2,3 and 4*. The frequency of the alternating current was 50 cycles/sec. Fig. 2 shows the structure of a nickel deposit obtained at a direct current density of 2 amp/sq.dm without superimposed a.c. The deposit shown in Fig.3 was formed at a direct current density of 2 amp/sq.dm with superimposed 50 cycles/sec a.c. of the same density. For the deposit shown in Fig.4, the d.c. density was 2 amp/sq.dm and the a.c. density was 3 amp/sq.dm.

As will be seen from the photographs, in the range of a.c. density 1-2 amp/sq.dm there is no appreciable increase in the size of the crystals of the deposit, but at an a.c. density of 3 amp/sq.dm the grain size increases sharply. It is evident that this increase in crystal size is to be observed only when the value of the superposed alternating current exceeds that of the direct current.

Besides studying the structures of electrolytic deposits of nickel, we examined the effect of the superposition of an alternating current on the porous character of the deposits. In these investigations electrolytic deposits of nickel were obtained from electrolyte of the same composition of a d.c. density of 2 amp/sq.dm, the a.c. density being varied from 1 to 3 amp/sq.dm. The thickness of the deposit investigated was 18-20 μ. The number of pores was determined by the aid of a reagent of the following composition:

---

*We express our gratitude to A. B. Shekhter and I. I. Tretyakov for the determination of the microstructures of the deposits with the aid of the electron microscope. See Plate, p. 547.

$K_4Fe(CN)_6$ . . . . 20 g/liter
NaCl . . . . 10 g/liter

The reagent was allowed to act for 2 min. The pores were counted under the microscope at a magnification of 50 [8]. The experimental results are given in Table 1.

TABLE 1

Dependence of the Pore Density* on the Relative Densities of the Direct and Alternating Currents (frequency of a.c, 50 cycles/sec)

D.c. density (amp/sq.dm)	A.c. density (amp/sq.dm)			
	0	1	2	3
	Number of pores per sq.cm			
1	20	8	10	16
2	14	8	9	14
3	16	7	11	13

---

* The pore density results given in Table 1 are average values from 18 experiments.

TABLE 2

Dependence of Pore Density on the Frequency of the Alternating Current

D.c. density (amp/sq.dm)	A.c. density (amp/sq.dm)	A.c. frequency (cycles/sec)					No. of pores per sq.cm without superposition of a.c.
		20	50	500	4000	12000	
		Number of pores per sq.cm					
1	1	7	8	10	17	18	20
2	1	7	8	11	14	13	14
3	1	9	8	8	14	15	16

As will be seen from these results, when an alternating current of density of 1-2 amp/sq.dm is superimposed, the number of pores diminishes sharply. Besides studying the effect of the density of the alternating current, we investigated the effect of the frequency of the current on the porous nature of the electrolytic deposits of nickel. Table 2 shows the dependence of the pore density on the frequency of the alternating current. As will be seen from Table 2, a high-frequency alternating current has no effect on the pore density of electrolytic deposits of nickel.

DISCUSSION OF RESULTS

It is evident that, when there is a superimposed alternating current of density greater than that of the direct current, conditions are created at the cathode that lead not only to intensive growth in the nickel crystals formed, but also to their periodic dissolution in association with the changing direction of the alternating current. If it is assumed that the electrolytic deposit on the cathode consists of crystals of variable size (which is indeed so in most cases, see Fig.2), then it may be supposed that when the direction of the current changes there will be preferential dissolution of the fine crystals, owing to their greater excess of surface energy and therefore lower stability when compared with the larger crystals.

The dependence of solubility on surface energy and on crystal dimensions is given by Thomson's equation:

$$RT \ln \frac{p_2}{p_1} = \frac{2\sigma M}{d} \cdot \frac{1}{r_2} - \frac{1}{r_1}, \qquad (1)$$

where p_2 is the vapor pressure of crystals of radius r_2, p_1 is the vapor pressure of crystals of radius r_1; σ is the surface tension of the crystals, $\underline{M}$ is the molecular weight, and $\underline{d}$ is the density of the metal. Denoting the L.H.S. of equation 1 by η, the overvoltage, [9] and assuming r_1 to be sufficiently great, we obtain:

$$\eta = \frac{2\sigma M}{dnF} \cdot \frac{1}{r_2}. \qquad (2)$$

The determination of the dissolution rates for crystals of various dimensions from this formula is difficult, firstly owing to the absence of exact data on the surface tension of the crystals of solid metal, in particular nickel, and secondly owing to the difficulty of establishing the exact relationship between the overvoltage and the crystal dimensions.

Analogous calculations from equation 2 for the deposition of silver [9] have shown that for a ten-fold change in crystal dimensions ($r' = 1.4 \cdot 10^{-5}$ and $r'' = 1.4 \cdot 10^{-4}$), the overvoltage for silver deposition changes by only 1.7 mV. When it is considered that the order of magnitude of the overvoltage for dissolving nickel crystals scarcely changes in comparison with that of silver with variation in crystal dimensions, it is evident that the overvoltage arising from differences in the crystal dimensions in nickel is very small in comparison with the total overvoltage observed in the electrodeposition of nickel [10]. It may therefore be considered that variations in the rate of dissolution of crystals due to variations in size cannot play an important part in the electrodeposition of nickel, and it is thus impossible to explain the increase in size of nickel crystals when alternating current is superimposed as the result merely of preferential dissolution of small crystals.

Another possible explanation is as follows. When electrodeposition of nickel occurs in the course of electrolysis, there occurs the discharge not only of nickel ions, but also of hydrogen ions, with the result that colloidal particles of hydroxide are formed directly at the surface of the electrode, particularly in neutral or weakly acid solutions [11]. These particles, which separate at the cathode together with the depositing metal, act as passivators, hindering the growth of the nickel crystals. As a result of this inhibition of crystal growth, a finely crystalline nickel deposit is obtained. According to Billiter [12], these particles (passivators) may be detected in the form of black embedded matter at the boundaries of the grains by examination of metallographic preparations of the deposit.

The formation of finely crystalline deposits of nickel resulting from the action of the hydroxide, which is formed at the cathode and becomes embedded in the deposit, has been noted also by other authors [13]. In fact, when the nickel deposit is analyzed, a certain amount of oxygen can be detected, which confirms that the embedding of hydroxide in the deposit has occurred [12-14].

On the basis of the above discussion it may be regarded as probable that the formation of a finely crystalline structure in the electrodeposition of nickel is due to inhibition of crystal growth. The superposition of alternating current in the electrodeposition of nickel must reduce the effect of these passivators, since the electrode is polarized alternately cathodically and anodically — when polarization is anodic, the hydroxide particles not only cannot separate at the electrode owing to their positive charge, but will even move away from the electrode,. On the other hand, owing to the anodic polarization of the electrode, the discharge of hydroxyl ions will occur there, leading to acidification of the solution adjacent to the electrode. Increase in the acidity of the layer adjacent to the cathode will result in the destruction of the hydroxide particles that have formed. These two processes will result in a reduction in the concentration of the hydroxide, i.e. of the inhibitor of crystal growth.

The high overvoltage value for the electrodeposition of nickel is to be explained by the difficulty, due to the inhibiting effect of adsorbed nickel hydroxide on the electrode surface, of discharging nickel ions [10]. The lowering of the overvoltage by the superposition of alternating current is to be explained by the partial removal of the nickel hydroxide.

On the basis of this discussion it is evident that, as the factors causing passivation of the crystals are removed, conditions are created that encourage the growth of individual crystals, and the factors preventing coalescence of crystals are removed also. Curtailment of the growth of a group of growing crystals appears to be one of the causes of the formation of pores between them [8].

Reduction in the number of pores when alternating current is superimposed is to be explained by a reduction in the adsorption of the passivators (nickel hydroxide) that inhibit the growth and coalescence of the growing crystals and prevent the formation of more compact deposits. The absence of any effect due to the alternating current on the number of pores in electrolytic deposits of nickel when the frequency is increased may be explained by the fact that at high frequencies the composition of the solution in the cathodic layer does not alter — acidification and the removal of hydroxide particles from the cathode layer do not occur owing to the high frequency with which the direction of the current changes [15].

SUMMARY

1. The effect of alternating current on the electrodeposition of nickel has been studied. It has been shown that, when alternating current of greater than a certain density is superimposed, the deposit is of a coarsely crystalline structure.

2. It has been shown that, when alternating current is superimposed, the number of pores in electro-

lytic deposits of nickel is reduced. With increase in the frequency of the alternating current, its effect gradually disappears.

3. A hypothesis is given in the paper concerning the possible mechanism of the action of alternating current on the structure of the deposit and also on the overvoltage for the discharge of nickel ions.

Received December 28, 1951

Institute of Physical Chemistry of the
USSR Academy of Sciences

LITERATURE CITED

[1] V. I. Melik-Gaykazyan and P. L Dolin. New Methods for the Physico-chemical Investigation of Surface Phenomena. Trans. Inst. Phys. Chem., No. 1. Acad. Sci. USSR Press, 1950; M. A. Proskumin and M. A. Vorsina. Proc. Acad. Sci. USSR 24, 915 (1939); M. A. Proskurin and A. N. Frumkin, Trans.Far. Soc. 31, 110 (1935).

[2] B. V. Ershler. Trans. Second Conference on Corrosion of Metals. Acad. Sci. USSR Press. Part II., 1943.

[3] P. L Dolin and B. V. Ershler. J. Phys. Chem., 14, 886 (1940).

[4] F. Halla, Z. Elektrochem. 35, 842, 1929; A. Brochet and J. Petit, Z. Elektrochem. 10, 909 (1904).

[5] N. A. Izgaryshev and S. S. Berkman, Z. Elektrochem. 31, 10 (1925); N. A. Izgaryshev and N. T. Kudryavtsev, Z. Elektrochem. 38, 131 (1932).

[6] V. Kohlschutter and Schodl, Helv. chim. Acta 5, 490, 593 (1922).

[7] G. T. Bakhvalov. Trans. Second All-Union Conference on Theor. and Applied Electrochem. Acad. Sci. USSR Press, Kiev, 1949.

[8] A. A. Sutyagina and A. T. Vagramyan. J. Appl. Chem., 24, 945 (1951).*

[9] A. T. Vagramyan. Electrodeposition of Metals. Acad. Sci. USSR, 1950.

[10] A. T. Vagramyan and Z. A. Solovyeva. Proc. Acad. Sci. USSR, 77, 629 (1951).

[11] G. S. Vozdvizhensky. J. Appl. Chem., 20, 813 (1947); M. N. Polukarov. J. Gen. Chem., 19, 1583 (1949)**; V. Kuznetsov. J. Phys. Chem., 24, 574 (1950).

[12] Zh. Billiter. Fundamentals of Galvanotechnics. United Sci.-Tech. Press, 1937.

[13] K. M. Gorbunova, T. V. Ivanovskaya, and N. A. Shishakov. J. Phys. Chem., 25, 981 (1951).

[14] D. J. Macnaughtan and A. W. Hothersall, Trans. Far. Soc. 24, 497 (1928); 387 (1928); D. J. Macnaughtan and R. A. F. Hammond, Trans. Far. Soc. 26, 481 (1930); 27, 633 (1931); A. K. Gardam and D. J. Macnaughtan, Trans. Far. Soc. 29, 753 (1933).

[15] N. I. Stepanov. Bull. Acad. Sci. USSR, 8, 1395 (1914); M. Leblanc and K. Schick, Z. phys. Chem. 46, 213 (1903); Z. Elektrochem. 16, 25 (1910).

---

* See Consultants Bureau translation, p.1025

** See Consultants Bureau translation, p. a-1.

A STUDY OF OXYGEN EXCHANGE ON VANADIUM CATALYSTS BY THE USE OF O^{18}

L. Ya. Margolis and E. G. Plyshevskaya

Several papers have appeared recently in the literature concerning the application of heavy oxygen to the study of the mechanism of oxidation reactions. Karpacheva and Rozen [1] consider that the ability of catalysts to undergo oxygen exchange is related to their catalytic activity. In investigations of oxygen exchange on copper oxide, manganese dioxide, and vanadium pentoxide at 200-450° they established that in all these cases oxygen exchange occurs. In 1940 Morita [2] published work in which he showed that on manganese dioxide at 400° there is oxygen exchange amounting to about 20%, but on copper oxide there is no oxygen exchange to be observed up to temperatures of 600-900°. In 1949 Allen and Lander [3] investigated oxygen exchange on copper (II) oxide, cobalt (III) oxide, and nickel (II) oxide, which were prepared by oxidation of metal foil with a mixture of O^{16} and O^{18} (O^{18} content of mixture: 1.4%), and they established that oxygen exchange begins at 600° on cobalt oxide and at about 400° on copper oxide. The authors maintained that there is a parallelism between the degree of oxygen exchange and the active surface of the catalyst.

On the other hand, Vaynshtein and Turovsky [4] in a study of the oxidation of carbon monoxide at MnO_2 asserted that oxygen exchange does not occur on a carefully dehydrated catalyst at 280°. Also, no exchange was detected with the reaction product — carbon dioxide. They explained the divergence between their results and those of Karpacheva and Rozen by the use by the latter of catalysts that had not been sufficiently freed from moisture. Presence of moisture in the catalysts facilitates oxygen exchange and makes it difficult to establish the true mechanism of the reaction. Owing to the existence of such contradictory data in the literature, it was essential, before studying the fundamental mechanism of the oxidation of hydrocarbons, to determine the degree of oxygen exchange on oxide catalysts of mild and severe oxidative effect. Oxygen exchange was studied at the temperature and for the time used in the oxidation reaction (350-450°).

EXPERIMENTAL

The exchange was studied under static conditions in the apparatus shown in Fig. 1. The gas passed from the gas collectors 31-35 into the manifold 3, and was introduced via the tap 10 into the reaction vessel 23. The latter was situated in an electric furnace 24, the temperature of which was maintained constant within 0.1° by the aid of a thermoregulator working in conjunction with a resistance thermometer.

The procedure was as follows: A weighed amount of catalyst (1-1.5 g) was placed in the reaction vessel, protected by means of solid carbon dioxide from grease vapor, and activated for several hours at 450°. The temperature required for the experiment was then established, and the catalyst was maintained at this temperature for an hour.

Heavy oxygen was obtained by the electrolysis of heavy-oxygen water, containing 0.9% O^{18}. The analysis of the oxygen was carried out before and after the exchange in the mass spectrometer. The oxygen was first mixed with carbon monoxide and burnt at a platinum wire in the reaction vessel 19 to give carbon dioxide, which was frozen out by means of liquid nitrogen in the tubes 28, which were fused off from the apparatus and placed in the mass spectrometer. As a result of the analysis, the enrichment of the carbon dioxide in $CO^{12}O^{18}$ in comparison with natural CO_2^{16} was determined. The enrichment coefficient for the orignal heavy oxygen was 2.35. The results of the mass-spectrometric analysis were accurate within 3-5%.

The exchange experiments were carried out by two methods:

1. Oxygen $O^{16} + O^{18}$ (0.9% O^{18}) was sorbed at catalyst that did not contain heavy oxygen. When sorption was complete, the residue of oxygen was pumped out, oxygen O^{16} was introduced into the gas phase, and this was maintained over the catalyst for 2 hrs.

2. Heavy oxygen was introduced into the catalyst by treating it with the vapor of heavy oxygen water at 450-500° in an apparatus for dynamic treatments. The O^{18} content of the catalyst was about 100 γ per g. This catalyst was maintained in an O^{18} atmosphere for 2 hrs. The reproducibility of the analytical results in the different experiments was quite satisfactory (see Table 1).

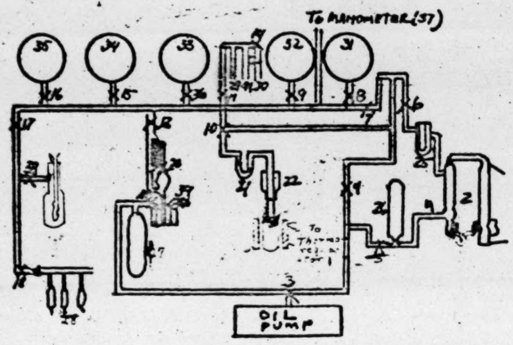


Fig. 1. Diagram of static apparatus for the study of oxygen exchange and the oxidation of hydrocarbons with heavy oxygen: 1) oil fore-pump; 2) mercury diffusion pump; 3) manifold; 4-18, 36-40) stop-cocks; 19) reaction vessel for burning O_2 + CO; 20) McLeod gage; 21,22,25) traps for freezing out; 23) reaction vessel; 24) electric furnace; 26,27) fore-vacuum reservoirs; 28) tubes for freezing out CO_2; 25,29,30,41) traps for analysis; 31-35) gas collectors

Various oxidation catalysts were used:

1) V_2O_5, chemically pure, having the rhombic lattice parameters: a = 11.7; b = 4.36; c = = 3.56, (according to Ketelaar [5]: a = 11.48; b = 4.36; c = 3.55.

2) V_2O_4 prepared by the reduction of vanadium pentoxide in a stream of hydrocarbon for 420 min.

V_2O_4 has a tetragonal lattice having the parameters: a = 4.51; c = 2.87. The data in the reference book (Strukturberichte) are a = 4.54, c = 2.88.

3) Magnesia-chrome catalyst: $MgCr_2O_4 + MgO$.

1. Sorption of Oxygen

In the work of Karpacheva and Rozen [1], a relation was found between oxygen exchange and activated sorption. The authors supposed that activated sorption is probably a stage of the exchange process, and they brought forward data concerning the parallelism between the degree of sorption and the extent of oxygen exchange. The extent of the exchange is closely related to the mobility of oxygen in the lattice and to the catalytic activity of the material. Therefore, in connection with an investigation of oxygen exchange on catalysts of mild and severe oxidative effect it is desirable to study the sorption of oxygen on them at the temperatures of the oxidation reaction. The isotherms for the sorption of oxygen on V_2O_5 and V_2O_4 for 250, 350 and 450° are given in Figs. 2,3,4 and 5. At these temperatures the sorption of oxygen is irreversible (Fig.6); the character of the isotherms shows that activated sorption of oxygen occurs on all these catalysts.

TABLE 1

Reproducibility of Results on Oxygen Exchange on Vanadium Pentoxide

No.	Catalyst	Temp. °C	Enrichment coefficient $CO^{18}O^{16}/CO_2^{16}$	Note
1	V_2O_5	350	1.0	Enrichment coefficient of original $CO^{18}O^{16}$ = 2.36
2	Ditto	350	1.0	
3	V_2O_5 containing O^{18} (100 γ/g)	350	1.0	
4	Ditto	350	1.0	
5	″	450	1.04	
6	V_2O_5 having sorbed O^{18} . . .	450	1.04	
7	V_2O_5 containing O^{18} (100 γ/g)	450	1.05	
8	Ditto	450	1.05	

We have previously [6] studied the sorption of oxygen on magnesium chromite, a typical catalyst for far-reaching oxidation of hydrocarbons. For this catalyst we found a relation between the activation energy and the degree of sorption. The distribution of surface sites in accordance with their activation energies obeyed an exponential law. If we represent the kinetic sorption curves obtained for the sorption of oxygen on V_2O_5 in bilogarithmic coordinates (log q, log t), all points are found to lie on a straight line over a range of times extending over three orders of magnitude (Fig. 7). In other words, the kinetics of the activated sorption of oxygen follow

Benham's equation

$$q = At^{1/n},$$

where $1/n = \alpha RT$

$$A = f(T)$$

or

$$A = \frac{H}{\alpha(\tau_0)^{1/n}},$$

where $\underline{t}$ is time; $\underline{n}$ and $\underline{H}$ are constants; $\underline{R}$ is the gas constant; $\underline{T}$ is the temperature;

$$\tau = \frac{1}{k_0 p^s},$$

where k_0 is a factor that enters into the rate constant; and $\underline{p}$ is the pressure.

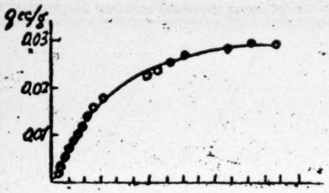


Fig. 2. Isotherm for sorption of oxygen on V_2O_5 at 250°

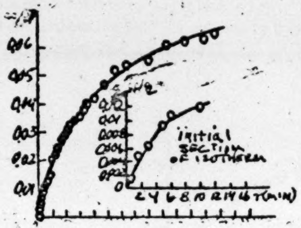


Fig. 3. Isotherm for sorption of oxygen on V_2O_5 at 250°

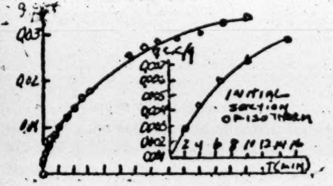


Fig. 4. Isotherm for sorption of oxygen on V_2O_5 at 450°

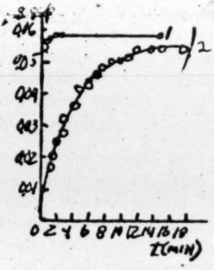


Fig. 5. Isotherm for sorption of oxygen on V_2O_5 at 350°; 1) dehydrated, 2) in present of moisture

As Roginsky has shown [7], this is the typical kinetic equation for activated sorption on a heterogeneous surface characterized by an activation energy distribution function of exponential form for the adsorption process. In Fig. 8 the distribution function $\rho(E)$ is expressed in terms of the logarithm to base 10 of time, the change of which is proportional to the change in activation energy for the process of activated sorption: $E \approx RT \log \underline{t}$.

The number of active sites rises with increase in the activation energy both for $MgCr_2O_4$ and for V_2O_5 (see Fig. 8 and 9, curves 1 and 2). The rate of sorption of oxygen on V_2O_4 is considerably greater than on V_2O_5. In Fig. 4 and 5 the isotherms of sorption of oxygen on V_2O_5 and V_2O_4 at 450° are given. Vaynshteim and Turovsky point out that presence of moisture in the pores of the catalyst considerably facilitates oxygen exchange between the catalyst and the gas phase at 180-200°. It was necessary to determine the effect of moisture in the catalyst on the sorption of oxygen.

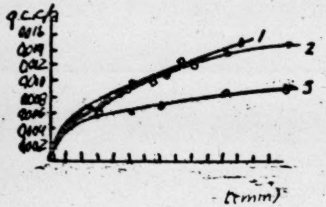


Fig. 6. Reversibility of sorption of oxygen on V_2O_5 (low activity) at 300°; 1) sorption isotherm (expt. 1) 2) sorption isotherm for oxygen in presence of moisture, 3) sorption isotherm (expt. 2)

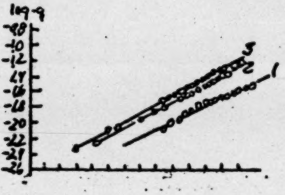


Fig. 7. Sorption isotherms for oxygen at V_2O_5 in bilogarithmic coordinates (log q and log t): 1) sorption isotherm at 250°, 2) sorption isotherm at 350°, 3) sorption isotherm at 450°

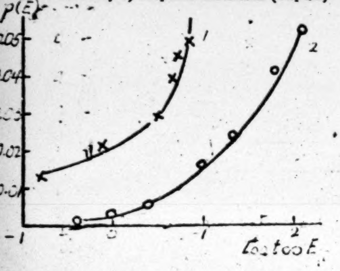


Fig 8. Dependence of the activation energy distribution function for the sorption of oxygen on log t∞E: 1) $MgCr_2O_4$; 2) V_2O_5.

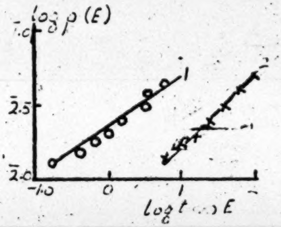


Fig. 9. Distribution function $\rho(E)$ expressed in co-ordinates $\log\rho$ and log t: 1) for $MgCr_2O_4$; 2) for V_2O_5

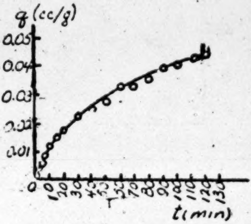


Fig. 10. Sorption isotherm for oxygen on V_2O_5 at 350° in presence of moisture.

Moisture was introduced into the catalyst in the following manner: A drop of water was frozen in the trap 41 by the aid of liquid nitrogen, the catalyst was carefully activated, and the water was then thawed and allowed to pass to the reaction vessel, where it was absorbed by the catalyst. Residual aqueous vapor was rapidly pumped off. The sorption isotherms for dehydrated V_2O_5 in presence of moisture are given in Fig.4. The amount of sorbed oxygen at a given temperature is reduced in presence of moisture. Experiments were carried out on V_2O_4 (Fig.10) which showed that presence of moisture in the catalyst reduces sorption of oxygen. This change in the sorption points to the blocking by the water of active sorption centers.

Thus, on passing from V_2O_5 to V_2O_4, we find a considerable increase in the sorption of oxygen at 350-450°. On the other hand, presence of moisture on the surface of the catalyst reduces both the amount of sorbed oxygen and the rate of sorption. The surfaces of vanadium catalysts and of magnesium chromite are heterogeneous with respect to the activation energy for the sorption of oxygen. The form of the distribution function for activation energies is the same for both types of catalyst. Consequently, both on V_2O_5, and also on magnesium chromite, there is an assembly of sites of varying activation energy for the sorption of oxygen, which participate in a varying manner in the catalytic oxidative process. Nevertheless, it is doubtful whether the heterogeneity of the surface with respect to activated sorption of oxygen can explain the differences in the course of the oxidation of hydrocarbons (mild and far-reaching reaction). Study of oxygen exchange on these catalysts ought to give an idea of the mobility of oxygen on the surface during the oxidation reaction.

2. Oxygen Exchange on Various Oxidation Catalysts

The results on oxygen exchange on vanadium pentoxide, on vanadium tetroxide, and on magnesia-chrome catalyst are given in Tables 1 and 2. The O^{18} content in natural carbon dioxide is taken as the unit. If the coefficient for enrichment in $CO^{16}O^{18}$ is unity, then there is no exchange between the oxygen of the gas phase and the oxygen of the catalyst.

TABLE 2

Exchange between Oxygen in the Catalyst and Gaseous Oxygen

No.	Catalyst	Temp. °C	Enrichment coefficient $CO^{16}O^{18}/CO_2^{16}$		
			H_2O absent	H_2O present	CO_2^{18} present
1	V_2O_5 containing O^{18}	350	1.0	—	1.0
2	V_2O_4 containing O^{18}	350	1.13	1.22	1.10
3	$MgCr_2O_4$ containing O^{18}	350	1.0	—	1.0
4	Silver catalyst	270	1.05	—	—

Hence, in absence of moisture and in presence of the reaction product CO_2^{18} sorbed on the catalyst at 350°, oxygen exchange is not observed on V_2O_5 and on $MgCr_2O_4$. On V_2O_4 under the same conditions oxygen exchange proceeds to an insignificant extent, the enrichment coefficient $CO^{16}O^{18}/CO_2^{16}$ being 1.13 and 1.10. The presence of moisture increases the oxygen exchange, but only slightly.

As a result of the oxidation of hydrocarbons at the surface of the catalyst, moisture will always be present and oxygen exchange will consequently occur. From the oxygen exchange we may evaluate the extent of desorption of oxygen from the catalyst at the reaction temperature; as the results show, the extent to which desorption occurs is not great. In every oxidative process in presence of oxygen in the gas phase and on the surface of the catalyst, two reactions proceed simultaneously: 1) oxidation at the surface by the oxygen of the catalyst, 2) oxidation by oxygen from the gas phase.

The rates of these two reactions are different on mild-oxidation catalysts and on catalysts that promote far-reaching oxidation. It is probable that the mobility of oxygen during reaction is not the same as when hydrocarbon is absent. The specificity of oxidation catalysts cannot be explained by the degree of oxygen exchange at 350-450°. Only by a study of the kinetics of oxygen exchange on various catalysts will it be possible to establish the relation between the activity of oxidation catalysts and the extent of oxygen exchange.

SUMMARY

1. The kinetics of activated sorption of oxygen on vanadium catalysts at 250-400° have been studied.

2. It has been shown that the surface of vanadium catalysts is heterogeneous with respect to the activation energies of oxygen sorption.

3. A mass-spectrometric method of analysis has been applied to the study of oxygen exchange at catalysts containing heavy oxygen.

4. Oxygen exchange has been studied on catalysts of mild and far-reaching oxidative effect at the temperature of the oxidation reaction (350-450°).

Graduate T. V. Bykova took part in the work.

Received November 1, 1951

Institute of Physical Chemistry of the
USSR Academy of Sciences

LITERATURE CITED

[1] S. M. Karpacheva and A. M. Rozen. Proc. Acad. Sci. USSR, 68, 1057 (1949); 75, 239 (1950).

[2] M. Morita, Bull. Chem. Soc. Japan 14, 520 (1940).

[3] J. Allen and J. Lander, Nature 164, 142, 1130 (1949).

[4] D. M. Vaynshtein and G. Ya. Turovsky. Proc. Acad. Sci. USSR, 72, 297 (1950).

[5] A. Ketelaar, Nature 137, 316 (1936).

[6] L. Ya. Margolis. Bull. Acad. Sci. USSR. Div. Chem. Sci., No. 3, 262 (1951).

[7] S. Z. Roginsky. Adsorption and Catalysis at Heterogeneous Surfaces. Moscow 1948.

BLANK
PAGE

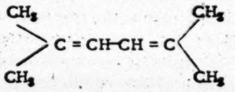
CATALYTIC HYDROGENATION OF DOUBLY UNSATURATED COMPOUNDS HAVING A CONJUGATED SYSTEM OF DOUBLE BONDS

COMMUNICATION 1. HYDROGENATION OF BIISOCROTYL

B. A. Kazansky and N. I. Popova

Lebedev [1] expressed the opinion that addition of hydrogen to conjugated dienes in presence of a catalyst (platinum black) may proceed in various ways, according to the structure of the diene, and he proposed that dienes should be divided accordingly into the following four types.

Type I. Hydrogenation of dienes of this type proceeds in strictly selective fashion in two stages. In the first stage addition of hydrogen occurs exclusively in the 1,4-positions of the conjugated system with formation of an ethylene compound having a double bond between atoms 2 and 3 of the original conjugated system, i.e. the first stage of hydrogen addition goes exclusively according to Thiele's rule. The curve representing this process should have a sharp break corresponding to the moment at which addition of the first hydrogen molecule is complete and should be reminiscent in form of the hydrogenation curve for a binary mixture of ethylenic compounds differing in degree of substitution, which will hydrogenate successively at different rates. Lebedev supposed that compounds of type I include compounds in which all four hydrogen atoms on the first and fourth carbon atoms of the conjugated system (1,3-butadiene) are replaced by aliphatic radicals. An example of such compounds is biisocrotyl (2,5-dimethyl-2,4-hexadiene):



$$(CH_3)_2C=CH-CH=C(CH_3)_2$$

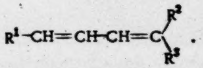
It must be remarked, however, that Lebedev, while ascribing biisocrotyl to the first type of dienes, brought forward no experimental data in support of this view and, in particular, gave neither a hydrogenation curve, nor an analysis of the reaction products.

Type II. In this case addition of hydrogen does not proceed in selective fashion, and the reaction proceeds in all possible directions, i.e. in the 1,2-, 3,4-, and 1,4-positions of the conjugated system; also, complete hydrogenation occurs. In this case the process does not go according to Thiele's scheme, and the reaction rate curves have a very complex form. For example, the curves for the hydrogenation of piperylene and 1,3-butadiene each have three distinct sections; the curve for isoprene has four. Also, addition of one molecule of hydrogen to a compound of this type is not accompanied by a change in the number of active components in the mixture undergoing hydrogenation. The kinetic curves for the reaction do not therefore show a break at this point; the break occurs considerably later — when 65-70% of the amount of hydrogen required for complete saturation of the system has been added — and corresponds to the disappearance of the initial conjugated diene. Lebedev called this point "the critical point for hydrogenation of the conjugated system". All substances whose hydrogenation was studied by Lebedev belong to type II, i.e. 1,3-butadiene, isoprene, piperylene, 2,3-dimethyl-1,3-butadiene, and others.

Type III. Lebedev referred to this type as being theoretically possible, but never observed in any of his experiments. In this case the hydrogen must add all at once to the extent of two molecules to give the saturated compound. During the whole hydrogenation process the reaction products must consist of a mixture of the fully hydrogenated substance and the original diene in various proportions. Hydrogenation curves for substances of type III will not have breaks, but will be reminiscent of the hydrogenation curves of individual mono-olefins.

Type IV. 1,4-Addition of hydrogen to the conjugated system in compounds of this type does not take place at all. The separate double bonds are hydrogenated on their own and independently, as in non-conjugated diene systems. Within this type Lebedev supposed two subtypes to be possible.

Type IVA. The double bonds differ in degree of substitution:



$$R^1-CH=CH-CH=C\begin{matrix}R^2\\ \\R^3\end{matrix}.$$

In this case they are saturated by hydrogen at differing rates, and the hydrogenation curve will show a break at the point for the addition of one molecule of hydrogen. In general, the curve for this type is reminiscent in form of that for type I, with the difference that the mono-olefin formed in this case by addition of one molecule of hydrogen will be a product of 1,2-addition to the conjugated system. It should be noted that there is not a single example in Lebedev's work of a substance that undergoes hydrogenation according to type IVA.

Type IVB. In this case the double bonds are identical in degree of substitution:

$$R^1-CH=CH-CH=CH-R^2.$$

The two double bonds will hydrogenate simultaneously, and the hydrogenation curve will be reminiscent in form of that for a mixture of mono-olefins that are homogeneous with respect to degree of substitution. If the hydrogenation process is interrupted when the addition of one molecular proportion of hydrogen has occurred, the hydrogenation product will consist of a mixture of the original diene, mono-olefins (1,2 and 3,4 hydrogen addition products), and the fully saturated substance. Products of the 1,4-addition of hydrogen to the conjugated system will be absent among the products of incomplete hydrogenation. It is possible to regard 2,4-hexadiene as an example of this type; in fact, the hydrogenation curve for 2,4-hexadiene in presence of platinum black has, according to Lebedev, a break at the point corresponding to addition of 70% of hydrogen, but Lebedev does not give the analysis of reaction products that is necessary so that 2,4-hexadiene may be with certainty ascribed to type II or to type IVB. Thus, as already stated above, all the substances investigated by Lebedev must be ascribed to type II in the scheme of classification that he has proposed, for the addition to them of hydrogen in presence of platinum proceeds in all possible directions.

The statements by Vavon and coworkers [2] and by Ingold [3] that in the catalytic hydrogenation of compounds having conjugated double bonds it is possible for the conjugated system to become completely saturated in one step with formation of a mixture of the fully saturated compound and the non-hydrogenated compound (without intermediate formation of mono-olefins) have not been confirmed and were evidently the results of defects in the procedure used for the investigation of the reaction products. The observation of Paal [4], that in presence of colloidal palladium piperic acid goes direct to tetrahydropiperic acid, was not confirmed by Lebedev [5], who showed that both in presence and in absence of platinum black piperic acid is hydrogenated according to type II. The more recent work of Farmer and Galley [6] has shown that in the partial hydrogenation of doubly unsaturated acids having a conjugated system of double bonds hydrogen adds in several ways simultaneously, i.e. according to Lebedev's type II. The reaction products were analyzed by the aid of oxidation and ozonization reactions. It was shown also by Farmer and Hughes [7] that the course of the hydrogenation of these compounds depends on the nature of the catalyst and of the solvent. The ratio of reaction products varies somewhat with different catalysts; variation of the solvent affects only the rate of hydrogenation, and not the manner in which hydrogen addition occurs. In the experiments of Farmer and Hughes, palladium always showed a selectivity greater than that of platinum or of nickel.

Dupont and co-workers [8] studied the hydrogenation of isoprene and 2,3-dimethyl-1,3-butadiene in presence of Raney nickel. Analysis of the products of the hydrogenation of these hydrocarbons, with the aid of their Raman spectra, showed that addition of half of the total hydrogen equivalent to each of these leads to the formation both of olefins having the double bond in the 1,2-position and also of olefins having a 2,3-double-bond.

Young and co-workers [9] showed that butadiene, in full agreement with Lebedev's results, hydrogenates according to type II in presence of one of the following four catalysts: platinum (from the oxide), palladium (from the oxide), palladium (deposited on barium sulfate), and Raney nickel. The lower selectivity of hydrogenation in presence of platinum, as compared with palladium, was observed also by Young. Also, Young showed that in the hydrogenation process it is possible for the double bond in a mono-olefin to undergo migration; thus in the hydrogenation of 2-butene to an extent of about 20% in presence of the catalysts $Pd/BaSO_4$, it was found that the unhydrogenated residue consisted of 8% and 92% 2-butene. In the 50% hydrogenation of 2-butene, isomerization again occurred; the composition of the butene residue was 8.5% 1-butene, 20.5% cis-2-butene, and 71% trans-2-butene. If such double-bond migration is a general phenomenon in the hydrogenation process for dienes, then it is impossible to form any opinion of the mechanism of the hydrogenation of dienes or to discover any regularities in this reaction that are related to the structure of the original substance.

This review of work on the catalytic hydrogenation of compounds having a conjugated system of double bonds shows that practically all such compounds are hydrogenated in a non-selective fashion, i.e. according to Lebedev's type II. Selectivity is to be observed in hydrogenation only when certain groups are present in the molecule (e.g. phenyl groups). Thus Kazansky and Tatevosyan [10] observed that both in the presence of platinum black, and also in presence of palladium black diphenylfulvene is hydrogenated selectively: the first two hydrogen molecules add at the two double bonds of the five-membered ring, and only then does addition of hydrogen at the remaining fulvene double bond begin. At the same time, dimethylfulvene, which has a structure similar to that of diphenylfulvene, does not show the same sharply defined selectivity when hydrogenated; this selectivity is evidently associated with the aromatic nature of the substituents on the extranuclear carbon atom.

The Lebedev types I, IVA, and IVB have remained without study from the experimental point of view. Hence, in 1940, Kazansky and Mikheev [11] subjected biisocrotyl, which belongs to type I, to catalytic hydrogenation in presence of platinum black. It was found that the hydrogenation curve for biisocrotyl did indeed show an inflection corresponding to the addition of one molecule of hydrogen; this gave some basis for the supposition that the process is selective and that, since the double bond system of biisocrotyl is of a symmetric nature, addition of hydrogen occurs primarily in the 1,4-positions. However, it was not found possible in 1940 to study the products of the addition of one molecule of hydrogen to biisocrotyl in detail, and the question of the order of this addition remained an open one.

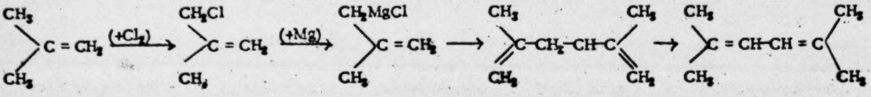
In the present work we have been able to make a more detailed investigation of this reaction, for we have had a much greater amount of biisocrotyl at our disposal and have been able to submit the hydrogenation products to precise fractionation. Also, the properties of 2,5-dimethyl-3-hexene, the product of the addition of one molecule of hydrogen to biisocrotyl at the 1,4-positions, were previously to be found only in Egloff's reference book [12], where reference is made to unpublished work without any indication of the method by which the hydrocarbon was prepared; only in 1950 was the synthesis of this hydrocarbon described [13]. Thus, only very recently has it become possible to carry out a chemical investigation into the products of the catalytic hydrogenation of biisocrotyl with sufficient confidence. The results of this investigation show that in presence of platinum black, of palladium black, or of Raney nickel the curves for the hydrogenation of biisocrotyl show a clearly defined break at the point corresponding to the addition of one molecule of hydrogen; this break is most clearly marked on the curve for hydrogenation in presence of palladium.

Nevertheless, in spite of this indication of the selectivity of the process, a detailed investigation into the composition and nature of the reaction products shows that in all cases the process proceeds non-selectively, i.e. in all possible directions, addition at the 1,2-positions of the conjugated system being, however, the most favored reaction (in all cases 2,5-dimethyl-2-hexene is the main reaction product). In the example we have taken there is a complete analogy, with respect to order of addition, between hydrogenation with catalytically activated hydrogen, that with hydrogen at the moment of its formation, and that with hydrogen that is adding under the influence of the sodium-liquid ammonia system [15]. It is evident that the order of addition of hydrogen to biisocrotyl is determined more by the structure of the molecule undergoing hydrogenation than by the nature of the hydrogen or of the catalyst. The effect of the latter is to be seen in the extent to which the saturated hydrocarbon is formed; it is less for palladium black, and particularly for Raney nickel, than for platinum. In this sense, hydrogenation of biisocrotyl proceeds in a less selective fashion on the last catalyst. Also, as will be seen later, the ratio between the amounts of hydrogen giving 1,2- and 1,4-addition, i.e. between the amounts of 2,5-dimethyl-2-hexene and of 2,5-dimethyl-3-hexene, also varies according to the nature of the catalyst. As regards migration of the double bond during catalytic addition of hydrogen to the diene, as found by Young in his work [9] (see above), in the case of the hydrogenation of biisocrotyl this phenomenon was not observed; this was proved by direct experiments on the partial hydrogenation of 2,5-dimethyl-2-hexene, when formation of 2,5-dimethyl-3-hexene, b.p. 102° was not detected; the first to distil off was 2,5-dimethylhexane, which has a considerably higher boiling point.

EXPERIMENTAL

1. The Synthesis of Biisocrotyl. Biisocrotyl was synthesized as indicated in the following scheme: (see top of next page)

Isobutene was chlorinated in the gas phase at room temperature [16]. The methylallyl chloride so obtained had b.p. 70-71° at 740 mm; n_D^{20} 1.4277; d_4^{20} 0.9258. By the action on this of metallic magnesium in absolute ether, 2,5-dimethyl-1,5-hexadiene was obtained in 84% yield: b.p. 113.7-114.0° at 758 mm; n_D^{20} 1.4296; d_4^{20} 0.7428; found MR_D 38.30; calculated for $C_8H_{14}\Gamma_2$ MR_D 38.21.



2,5-Dimethyl-1,5-hexadiene was isomerized in presence of aluminum oxide at 225-230° into 2,5-dimethyl-2,4-hexadiene (biisocrotyl) [17]. By distillation of the catalyzate through a column of 40 theoretical plates, biisocrotyl (262.5 g) was isolated; it had the following constants: b.p. 134.2-134.5° at 750 mm; m.p. 14.6-14.8°; n_D^{20} 1.4780; d_4^{20} 0.7635; found MR_D 40.86; calculated $C_8H_{14}\ulcorner_2$ MR_D 38.21; increment of MR_D 2.65. [18]: b.p. 134.5° at 760 mm; m.p. 13.94°; n_D^{20} 1.4781; d_4^{20} 0.7615; found MR_D 40.97; calculated $C_8H_{14}\ulcorner_2$ MR_D 38.21, increment of MR_D 2.76.

2. Method of Hydrogenation and of Investigation of the Composition of the Reaction Products. Hydrogenation was carried out by Lebedev's method at ordinary temperature and pressure in a flask shaken at a rate of not less than 300 complete oscillations per min. The rate of hydrogen absorption was measured accurately by the aid of gas burets graduated in 0.2 mm divisions, readings being taken every 0.5 min. Platinum black and palladium black were prepared by Willstatter's method [19], and nickel was prepared from nickel-aluminum alloy by Adkins' method [20]. Each series of experiments was carried out with different portions of the same sample of catalyst; 96% alcohol was always used as solvent.

The addition products from one molecule of hydrogen and one of biisocrotyl were distilled off together with the alcohol from a Favorsky flask, the catalyst being first filtered off; their azeotropic mixtures with alcohol boil between 71 and 73° approximately. The alcohol present in the distillate was extracted by means of calcium chloride solution, and the mixture of hydrocarbons separated in this way was fractionated in a column designed for accurate rectification. The distillation curve indicated which hydrocarbons were present in the mixture; their identification and quantitative estimation in the fractions were based on the boiling points, densities, refractive indices, and bromine numbers of the fractions. From all these data it was possible to draw up a complete balance sheet for the hydrogenation reaction with the given catalyst.

3. Hydrogenation of Biisocrotyl in presence of Platinum Black. Two experiments were carried out with small amounts in order to obtain kinetic curves for the hydrogenation. The results are given in Table 1.

TABLE 1

Expt. No.	Amt. of hydrocarbon(g)	Amt. of catalyst(g)	Amt. of alcohol(ml)	Pressure(mm Hg)	Temp. °C	Vol. of hydrogen (ml)	
						calculated	absorbed
1	0.3130	0.050	20	750	23	145.3	145.2
2	0.2994	0.086	20	750	18	134.2	135.8

The course of hydrogenation in expt. 2 is shown by the curve in Fig.1. It will be seen from this curve that the first molecule of hydrogen adds at a fairly constant rate; the rate of hydrogenation then falls and is gradually reduced to a very low value. In expt. 1 hydrogenation proceeded in similar fashion, but at a lower rate. In order to make a detailed investigation of the composition of the products of the hydrogenation of biisocrotyl at the stage corresponding to addition of one molecule of hydrogen, two experiments were carried out. In each of these biisocrotyl (13 g) was dissolved in alcohol (100 ml), and platinum black (1 g) was added to the solution. When the hydrogenation reaction was complete, the mixture of hydrocarbons was washed free from alcohol and distilled through a column of 30 theoretical plates; the amount of the mixture taken for distillation was 22.45 g

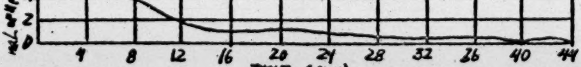


Fig. 1. Hydrogenation of biisocrotyl in presence of platinum black

(30.5 ml). The distillation curve is given in Fig.2.

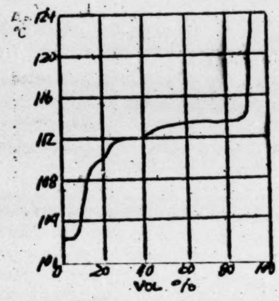


Fig.2. Distillation curve for the product of addition of one molecule of hydrogen to biisocrotyl in presence of platinum.

For each fraction collected determinations were made of refractive index, density, and bromine number (by Galpern and Vinogradova's modification [21] of Kaufmann's method). The results of all these determinations are given in Table 2. The bromine number of the pure mono-olefins (octenes) is 142.5.

The physical constants of the hydrocarbons that could be formed by partial and complete hydrogenation of biisocrotyl are given in Table 3.

From a consideration of the properties, including the bromine numbers, of the fractions obtained by distillation and from a consideration of the properties of the hydrocarbons given in Table 3, it is possible to calculate the composition of the mixture obtained by addition of one molecule of hydrogen to biisocrotyl:

2,5-Dimethyl-3-hexene . . .	13%
2,5-Dimethyl-2-hexene . . .	62%
2,5-Dimethylhexane	13%
Biisocrotyl	11%

TABLE 2

Fraction No.	B.p. (°C)	Pressure, (mm Hg)	n_D^{20}	d_4^{20}	Bromine No.	Olefin content of fraction %	Amt. of fraction, wt. %	Amt. of olefins, wt. %
1	102.1	760	1.4038	0.6990	143.1	100.4	6	6
2	102.1-109.8	760	1.4005	0.6778	90.5	63.5	11	7
3	109.8-109.9	760	1.4030	0.7037	84.3	59.2	3	2
4	109.9-112.0	760	1.4075	0.7084	95.6	67.1	18	12
5	112.0-113.2	760	1.4126	0.7146	126.6	88.8	15	13
6	113.2-113.3	760	1.4150	0.7182	143.8	100.9	32	32
7	113.3-126.5	760	1.4401	—	—	—	4	2
Residue in flask	—	—	1.4720	—	—	—	—	—
Residue in column	—	—	—	—	—	—	9	—
Losses	—	—	—	—	—	—	—	—

In the calculation it was assumed that fractions 1 and 2 contain 2,5-dimethylhexane and, of the olefins, 2,5-dimethyl-3-hexene; that fractions 3,4,5, and 6 contain 2,5-dimethylhexane and, of the olefins, 2,5-dimethyl-2-hexene; that fraction 7 consists of 50% 2,5-dimethyl-2-hexene and 50% biisocrotyl; and that the residue in the column consists entirely of biisocrotyl.

4. Hydrogenation of Biisocrotyl in presence of Palladium Black. Three experiments were carried out with different amounts of palladium black on the hydrogenation of biisocrotyl. The conditions of the experiments are shown in Table 4. The hydrogenation curve for expt. 3 is given in Fig. 3. It is similar in outward appearance to the curve for hydrogenation of biisocrotyl in presence of platinum, but the break corresponding to addition of one molecule of hydrogen is more marked. The character of the curve does not change with change in the amount of catalyst.

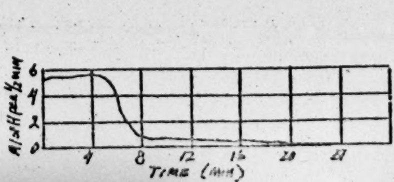


Fig. 3. Hydrogenation of biisocrotyl in presence of palladium black.

TABLE 3

Hydrocarbon	B.p. °C at 700 mm Hg	n_D^{20}	d_4^{20}	Literature Reference
2,5-Dimethyl-3-hexene	102.0-102.1	1.4030	0.7124	[12]
	103.5 (756 mm)	1.4100	0.7122	[13]
2,5-Dimethyl-2-hexene	112.0	1.4144	0.7190	[12]
2,5-Dimethylhexane	109.1	1.3925	0.6936	[22]

In order to make a detailed study of the products arising from the addition of one molecule of hydrogen to biisocrotyl, 75.45 g of this hydrocarbon was hydrogenated in several portions; for 10 g, 0.5-0.7 g of palladium black and 100-150 ml of alcohol were taken. According to calculation, for addition of one molecule of hydrogen to biisocrotyl under the conditions of the experiments 17.5 ml of hydrogen would be required. 18.4 ml was added, i.e. 1.04 mole of hydrogen. When the catalyst had been filtered off from the alcoholic solution, the latter was treated as previously described. The separated mixture of hydrocarbons was distilled through a column of 40 theoretical plates; 68 g (93.5 ml) of the mixture was taken for the distillation. The distillation curve is given in Fig.4, and the properties of the fractions are given in Table 5.

TABLE 4

Expt. No.	Amt. of hydrocarbon (g)	Amt. of catalyst (g)	Amt. of alcohol (ml)	Pressure (mm Hg)	Temp. °C	Vol. of hydrogen (ml)	
						calculated	absorbed
1	0.2960	0.05	20	745	23	137.2	136.9
2	0.3135	0.10	20	745	23	145.5	146.5
3	0.2710	0.06	20	745	23	126.4	126.5

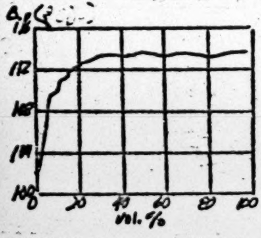


Fig.4. Distillation curve for the product of addition of one molecule of hydrogen to biisocrotyl in presence of palladium.

A simple examination of the distillation curve for the mixture of hydrocarbons formed as a result of addition of one molecule of hydrogen to biisocrotyl in presence of palladium black indicates that 2,5-dimethyl-2-hexene, b.p. 113°, predominates in this mixture to an appreciable extent. Calculation on the basis of data in Table 5 of the composition of the mixture yields the result:

2,5-Dimethyl-3-hexene . . . 6%
2,5-Dimethyl-2-hexene . . . 86%
2,5-Dimethylhexane 7%

5. Hydrogenation of Biisocrotyl in presence of a Raney Nickel Catalyst. Three experiments with Raney nickel catalyst were carried out under the conditions shown in Table 6.

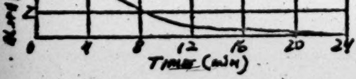


Fig.5. Hydrogenation of biisocrotyl in presence of a Raney nickel catalyst .

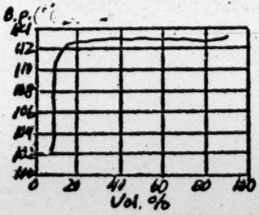


Fig.6. Distillation curve for the product of addition of one molecule of hydrogen to biisocrotyl in presence of nickel .

TABLE 5

Fraction No.	B.p. (°C)	Pressure, (mm Hg)	n_D^{20}	d_4^{20}	Bromine No.	Olefin content of fraction, %	Amt. of fraction, wt. %	Amt. of olefins, wt. %
1	102.2	760	1.4038	0.6990	144.8	101.7	2	2
2	102.0-109.7	760	1.3979	0.6972	73.6	51.7	8	4
3	109.7-112.7	760	1.4078	0.7115	109.0	76.5	15	12
4	112.7-113.2	760	1.4128	0.7168	145.6	102.2	16	16
5	113.2	760	1.4157	0.7183	145.4	162.2	55	55
Residue	–	–	1.4190	–	–	–	2	2
Losses	–	–	–	–	–	–	2	–

TABLE 6

Expt. No.	Amt. of hydrocarbon(g)	Amt. of catalyst(g)	Amt. of alcohol(ml)	Pressure(mm Hg)	Temp. °C	Vol. of hydrogen(ml)	
						calculated	absorbed
1	0.3310	0.2	25	750	27	155.5	Hydro-genation not carried out to comple-tion
2	0.3072	0.1	20	750	27	144.2	
3	0.2666	0.1	20	745	23	123.7	

TABLE 7

Fraction No.	B.p. (°C)	Pressure, (mm Hg)	n_D^{20}	d_4^{20}	Bromine No.	Olefin content of fraction, %	Amt. of fraction, wt. %	Amt. of olefins, wt. %
1	102.0	760	1.4045	0.6988	144.5	101.4	6	6
2	102.0-112.2	760	1.4044	0.7062	134.6	94.5	7	6
3	112.2-113.1	760	1.4143	0.7164	145.5	102.1	13	13
4	113.1-113.2	760	1.4157	0.7183	145.2	101.9	62	62
Residue in flask	–	–	1.4222	–	–	–	11	11
Residue in column	–	–	–	–	–	–	–	–
Losses	–	–	–	–	–	–	1	–

In Fig.5 we give the hydrogenation curve for expt. 2; the hydrogenation curves obtained in the other experiments were similar to this in character. They are all distinguished by the gentle character of the slope, as compared with the curves obtained in experiments with platinum and palladium; the break corresponding to addition of one molecule of hydrogen is not so marked, and the second molecule of hydrogen adds more and more slowly, so that it is rather difficult to cause hydrogenation to go to completion. When a large amount of catalyst is used (expt. 1), the curve has a short horizontal part and shows a rapid fall.

In order to make a study of the hydrogenation products, one molecular proportion of hydrogen was added to biisocrotyl (51 g). The mixture of hydrocarbons obtained after preparatory treatment as before was distilled through a column of 50 theoretical plates; altogether 48 g (66 ml) was distilled. The results of the distillation are shown in the curve of Fig.6 and in Table 7.

In the mixture formed by hydrogenation of biisocrotyl, 2,5-dimethyl-2-hexene predominates to an extent that is even greater than in the experiments with platinum and palladium,

In the calculation of the amounts of the separate hydrocarbons formed in the addition of one molecular proportion of hydrogen to biisocrotyl in presence of nickel, it was assumed that fraction 1 and 50% of fraction 2 consisted of 2,5-dimethyl-3-hexene and that fractions 3 and 4, 50% of fraction 2, and the residues in the flask and in the column consisted of 2,5-dimethyl-2-hexene. Fraction 2 contains also 2,5-dimethylhexane. The calculation gave the following result:

2,5-Dimethyl-3-hexene . . .	9%
2,5-Dimethyl-2-hexene . . .	90%
2,5-Dimethylhexane	1%

6. Experiments on the Isomerization of 2,5-Dimethyl-2-hexene. In order to find out whether 2,5-dimethyl-3-hexene is formed in our experiments as a result of secondary isomerization of 2,5-dimethyl-2-hexene in presence of catalyst and hydrogen, just as 1-butene in the experiments of Young and collaborators [9] underwent isomerization during its partial hydrogenation into 2-butene, we tried the addition to 2,5-dimethyl-2-hexene of 20-25% of the hydrogen necessary for saturation in presence of platinum black and of Raney nickel. Partial isomerization would have been readily observed since the 2,5-dimethyl-3-hexene that would be formed boils at 102°, i.e. 7° lower than 2,5-dimethylhexane and 10° lower than 3,5-dimethyl-2-hexene. The following results were obtained:

To 2,5-dimethyl-2-hexene (19 g), b.p. 112.5-113° at 755 mm; n_D^{20} 1.4153 and d_4^{20} 0.7182, isolated in the course of the partial hydrogenation of biisocrotyl in the previous experiments, 25% of the hydrogen required for complete saturation was added in presence of platinum black. The catalyzate was treated in the usual way and then distilled through a column of 40 theoretical plates. The first fraction boiled at 108° at 740 mm and had n_D^{20} 1.3950, i.e. was 2,5-dimethylhexane.

To 2,5-dimethyl-2-hexene (18.3 g) with the above-indicated properties 20% of the hydrogen necessary for complete saturation was added in presence of a Raney catalyst. In the distillation of the catalyzate through the same column, the first fraction boiled at 109.5° at 750 mm and had n_D^{20} 1.3950.

Thus, movement of the double bond to the center of the molecule with formation of 2,5-dimethyl-3-hexene did not occur either with a platinum or with a Raney nickel catalyst.

SUMMARY

1. Biisocrotyl, which, according to Lebedev, should be ascribed to type I in his proposed scheme for the classification of dienes, is hydrogenated in presence of platinum, palladium, and nickel in all possible ways, and must be ascribed therefore to type II.

2. In presence of each of these catalysts, 1,2-addition predominates.

3. The lowest selectivity in the addition of hydrogen is observed in presence of platinum, and the greatest in presence of nickel, when 90% of the hydrogenation product consists of 2,5-dimethyl-2-hexene (1,2-addition of hydrogen) and there is practically no formation of alkane.

4. In no case does the form of the curve for the rate of hydrogen addition indicate the characteristics of the actual course of reaction.

5. When 2,5-dimethyl-2-hexene is hydrogenated in presence of platinum or nickel, transposition of the double bond to the center of the molecule is not observed.

6. Variation in the amount of catalyst has no effect on the character of the hydrogenation curve.

Received January 5, 1952

Institute of Organic Chemistry
of the USSR Academy of Sciences

LITERATURE CITED

[1] S. V. Lebedev and A. I. Yakubchik. J. Russ. Chem. Soc., 59, 981 (1927).

[2] G. Vavon, Comptes. rend. 183, 299 (1926); Bull. (4) 41, 1253, 1598 (1927); G. Vavon, M. Jakes, Bull. (4) 41, 82 (1927).

[3] C. K. Ingold, L. D. Shah, J. Chem. Soc. 885 (1933).

[4] C. Paal, Ber. 45, 2221 (1912).

[5] S. V. Lebedev and A. I. Yakubchik. J. Russ. Chem. Soc., 61, 551 (1929).

[6] E. H. Farmer, R. Galley, J. Chem. Soc. 430 (1933).

[7] E. H. Farmer, L. A. Hughes, J. Chem. Soc. 1929 (1934).

[8] G. Dupont, C. Paquot, Comptes. rend. 205, 805 (1937).

[9] W. G. Young, R. L. Meier, J. Vinograd, H. Bollinger, L. Kaplan, S. L. Linder, J. Am. Chem. Soc. 69, 2046 (1947).

[10] B. A. Kazansky and G. T. Tatevosyan. J. Gen. Chem. 8, 1428 (1938); 9, 2248 (1939).

[11] B. A. Kazansky and E. P. Mikheev. Sci. Mem. Moscow State Univ., 71, 199 (1941).

[12] G. Egloff, Physical Constants of Hydrocarbons, 1, 227, 228, N. Y 1939.

[13] R. Ya. Levina, V. R. Skvarchenko, E. G. Treshchova, and V. M. Tatevsky, J. Gen. Chem., 20, 420 (1950). (See Consultants Bureau translation, p. 443).

[14] B. A. Kazansky and L. V. Gostunskaya, Proc. Acad. Sci. USSR, 71, 295 (1950).

[15] R. Ya. Levina and V. R. Skvarchenko. Bull. Moscow State Univ., No.10, 123 (1948).

[16] B. A. Kazansky and M. Yu. Lukina. Bull. Acad. Sci. USSR. Div. Chem. Sci., No.1, 47 (1951).

[17] R. Ya. Levina. J. Gen. Chem., 7, 1587 (1937).

[18] A. L. Henne, A. Turk, J. Am. Chem. Soc. 64, 826 (1942).

[19] R. Willstatter, Ber. 41, 2198 (1908).

[20] H. Adkins, V. Covert, J. Am. Chem. Soc. 51, 4116 (1929).

[21] G. D. Galpern and E. V. Vinogradova. Chem. Solid Fuel, 8, 384 (1937).

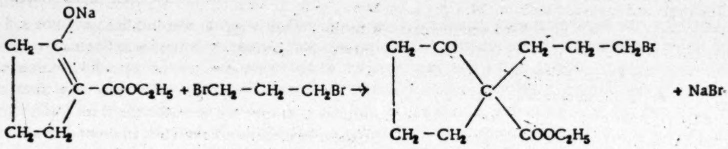
[22] F. Rossini, Selected Values of Properties of Hydrocarbons, Washington 1947, 40.

BLANK
PAGE

THE PREPARATION OF THE ETHYL ESTERS OF 1-(3-BROMOPROPYL)-2-OXOCYCLOPENTANECARBOXYLIC ACID AND OF 1-(3-CHLOROPROPYL)-2-OXOCYCLOPENTANECARBOXYLIC ACID

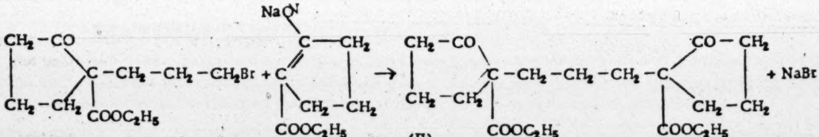
N.D.Zelinsky and N.V.Elagina

In order to prepare the ethyl ester of 1-(3-bromopropyl)-2-oxocyclopentanecarboxylic acid (I), which we required for our work, we carried out the reaction of 1,3-dibromopropane with the sodium derivative of the ethyl ester of 2-oxocyclopentanecarboxylic acid:



(I) (1)

We found that, when the reaction is carried out with equimolecular amounts of the reactants at room temperature, the yield of ethyl 1-(3-bromopropyl)-2-oxocyclopentanecarboxylate (I) is only about 20% of the theoretical. The low yield of (I) may be explained on the assumption that it reacts, as it is formed, with the sodium derivative of ethyl 2-oxocyclopentanecarboxylate with formation of the ester of a dicarboxylic acid (II):



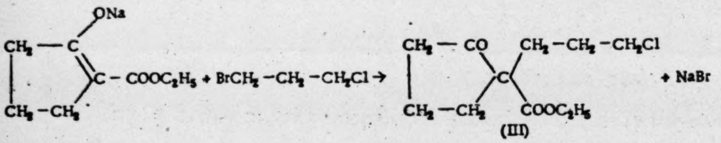
(II) (2)

Also, it is possible under the conditions of the experiment for the ester of 2-oxocyclopentanecarboxylic acid to be converted by the action of sodium ethoxide into the ester of adipic acid.

In an effort to raise the yield of the ester in which we were interested, we carried out the reaction between the sodium derivative of ethyl 2-oxocyclopentanecarboxylate and 1,3-dibromopropane using the latter in quantity $1\frac{1}{2}$ times that required by Equation (1). In order to avoid the splitting effect of sodium ethoxide on the oxocyclopentanecarboxylic ester, we took a somewhat smaller amount of sodium for the reaction than that required by theory, and we applied external cooling down to −15°. In this experiment the yield of ethyl 1-(3-bromopropyl)-2-oxocyclopentanecarboxylate was 32.2% of the theoretical.

In an experiment carried out with three times the theoretical amount of 1,3-dibromopropane, the yield of ethyl 1-(3-bromopropyl)-2-oxocyclopentanecarboxylate was raised to 46.3%. Four times the theoretical amount of the dibromopropane gave a 52.4% yield of the required ester. Thus, increase of the concentration of 1,3-dibromopropane in the reaction mixture inhibits Reaction 2 between ethyl 1-(3-bromopropyl)-2-oxocyclopentanecarboxylate and the sodium derivative of ethyl 2-oxocyclopentanecarboxylate and leads to increase in the yield of ethyl 1-(3-bromopropyl)-2-oxocyclopentanecarboxylate.

Ethyl 1-(3-chloropropyl)-2-oxocyclopentanecarboxylate (III) was obtained by us by the action of 1-bromo-3-chloropropane on the sodium deritative of ethyl 2-oxocyclopentanecarboxylate:


(3)

The yield of (III) in an experiment carried out with equimolecular amounts of the oxocyclopentanecarboxylic ester and the bromochloropropane was 67.8% of the theoretical.

The difference in the yields of the 1-(3-chloropropyl)- and the 1-(3-bromopropyl)-2-oxocyclopentanecarboxylic esters must be explained by the difference in reactivity of these compounds. The chloro derivative (III), owing to its lower reactivity in comparison with the bromo derivative (I), is less inclined to enter into reaction with the sodium derivative of the oxocyclopentanecarboxylic ester. The yield of ester (III) is therefore the greater.

EXPERIMENTAL

Ethyl 2-Oxocyclopentanecarboxylate

Dry toluene (600 ml) and metallic sodium (34.5 g; 1.5 g-atom) were introduced into a 2-liter round-bottomed flask fitted with a reflux spherical condenser that communicated with the air via a calcium chloride tube. The sodium was melted under the toluene and converted in the usual way into a fine powder. The flask was heated on an oil-bath, and, when the bath temperature reached 60°, diethyl adipate (303 g; 1.5 mole) was added quickly through the condenser. The temperature of the bath was allowed to rise slowly, and at 80° reaction commenced, which at 110° was accompanied by vigorous ebullition that continued for 15 minutes. During the reaction the flask was shaken vigorously several times. The sodium derivative of ethyl 2-oxocyclopentanecarboxylate came out as a voluminous mass. When the energetic reaction had finished, the flask was heated at 130° on the oil-bath for 1.5 hours.

The reaction mixture was cooled with ice and was decomposed with 10% acetic acid. The toluene layer was separated, and the aqueous layer was extracted with toluene. The united toluene solutions were washed with water, with a 7% solution of sodium carbonate, and again with water. The toluene was driven off, and the residue was vacuum-fractionated. The product was ethyl 2-oxocyclopentanecarboxylate (176.3 g; 75.3%), b.p. 83-84° at 5 mm.

Ethyl 1-(3-Bromopropyl)-2-oxocyclopentanecarboxylate (I)

The reaction between the sodium derivative of ethyl 2-oxocyclopentanecarboxylate and 1,3-dibromopropane was carried out in a 500-ml three-necked round-bottomed flask fitted with a mercury-sealed stirrer, a dropping funnel, and a reflux condenser protected from the moisture of the air by means of a calcium chloride tube.

Experiment 1. Absolute ethanol (80 ml) was introduced into the flask, and metallic sodium (4.4 g; 0.19 g-atom) was added gradually. When the sodium had dissolved, the flask was placed in an ice – salt cooling mixture, the temperature of which was maintained at about −15° throughout the reaction. Stirring was begun, and well-cooled ethyl 2-oxocyclopentanecarboxylate (31.2 g; 0.2 mole) was added slowly from a dropping funnel. When one-third of the total amount of ester had been added, its sodium derivative began to come out in white curds. The addition of the oxocyclopentane–carboxylic ester occupied 1 hour, and the mixture was then stirred for a further 1.5 hours. Strongly cooled 1,3-dibromopropane (60.5 g; 0.3 mole) was then rapidly introduced into the flask from the dropping funnel. When this addition was completed, stirring was continued for 1 hour with external cooling down to −15°. The mixture was then left overnight at room temperature. On the next day the reaction mixture, which had an alkaline reaction, was heated on a water bath maintained at 55-60°. The mixture was stirred for 5 hours, when a test made with moist litmus indicated a neutral reaction.

The reaction mixture, which was cooled with ice, was poured into ice water (400 ml), and the heavy light-yellow oil that settled on the bottom was separated. The aqueous layer was extracted with ether, and the ether extract was united with the oil already separated. The ethereal solution was washed with water and dried by means of anhydrous sodium sulfate. The ether was driven off, and the residue was vacuum-fractionated. Ethyl 1-(3-bromopropyl)-2-oxocyclopentanecarboxylate (17.1 g; 32.2% yield based on the sodium taken for reaction), b.p. 164-166° at 8 mm, was obtained as a result of repeated fractionation.

Experiment 2. Ethyl 2-oxocyclopentanecarboxylate (31.2 g; 0.2 mole), metallic sodium (4.3 g; 0.187 g-atom), and 1,3-dibromopropane (121.1 g; 0.6 mole) were taken for reaction, the experiment being carried out under the conditions used in the first experiment. After repeated vacuum-fractionation of the reaction products, ethyl

1-(3-bromopropyl)-2-oxocyclopentanecarboxylate (24.0 g; 46.3% based on sodium taken), b.p. 164-166° at 8 mm, was obtained.

Experiment 3. Ethyl 2-oxocyclopentanecarboxylate (31.2 g; 0.2 mole), sodium (4.4. g; 0.19 g-atom), and 1,3-dibromopropane (161.5 g; 0.8 mole) were caused to react under the same conditions as before. Vacuum-fractionation of the products yielded ethyl 1-(3-bromopropyl)-2-oxocyclopentanecarboxylate (27.8 g; 52.4% based on sodium taken), b.p. 164-166° at 8 mm.

Pure ethyl 1-(3-bromopropyl)-2-oxocyclopentanecarboxylate had the following constants: b.p. 134-135° at 2 mm; n_D^{20} 1.4915; d_4^{20} 1.3178; found MR_D 60.97; calculated $C_{11}H_{17}O_3Br$ MR_D 60.23.

Found %: C 47.63; 47.78; H 6.31; 6.31; Br 28.59; 28.77
$C_{11}H_{17}O_3Br$. Calculated %: C 47.66; H 6.18; Br 28.83;

Ethyl 1-(3-Chloropropyl)-2-oxocyclopentanecarboxylate (III)

The experiment was carried out in the apparatus described for the synthesis of ethyl 1-(3-bromopropyl)-2-oxocyclopentanecarboxylate. Ethyl 2-oxocyclopentanecarboxylate (78.0 g; 0.5 mole) and 1-bromo-3-chloropropane (78.7 g; 0.5 mole) were taken for reaction. A solution of sodium ethoxide was prepared by the dissolution of metallic sodium (10.7 g; 0.47 g-atom) in absolute ethanol (200 ml). The experimental procedure was the same as that used in the preparation of ethyl 1-(3-bromopropyl)-2-oxocyclopentanecarboxylate. The reaction products were vacuum-fractionated. Ethyl 1-(3-chloropropyl)-2-oxocyclopentanecarboxylate (73.4 g; 67.8% on basis of sodium taken), b.p. 122-124° at 2 mm, was obtained.

Pure ethyl 1-(3-chloropropyl)-2-oxocyclopentanecarboxylate had the following constants: b.p. 134.5-135.5° at 4 mm; n_D^{20} 1.4718; d_4^{20} 1.1329; found MR_D 57.50; calculated $C_{11}H_{17}O_3Cl$ MR_D 57.33.

Found %: C 56.62; 56.62; H 7.35; 7.46; Cl 14.84; 14.86;
$C_{11}H_{17}O_3Cl$. Calculated %: C 56.77; H 7.36; Cl 15.24.

SUMMARY

1. A study has been made of the reactions of the sodium derivative of ethyl 2-oxocyclopentanecarboxylate with 1,3-dibromopropane and with 1-bromo-3-chloropropane.

2. The ethyl esters of 1-(3-bromopropyl)-2-oxocyclopentane-carboxylic acid and of 1-(3-chloropropyl)-2-oxocyclopentanecarboxylic acid have been prepared.

Received December 17, 1951

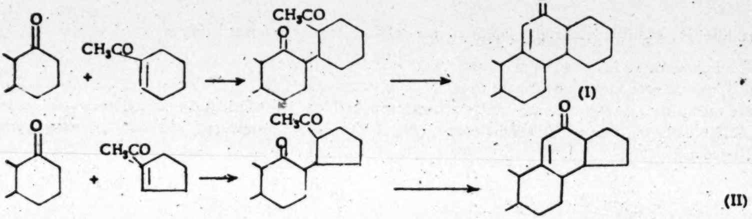
N.D.Zelinsky Organic Chemistry Laboratory
M.V.Lomonosov Moscow State University

SYNTHESIS OF POLYCYCLIC COMPOUNDS RELATED TO STEROIDS

XIII. REACTION OF CARBOCYCLIC KETONES WITH 1-ACETYL-1-CYCLOHEXENE

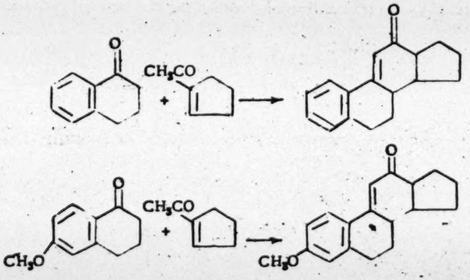
I.N.Nazarov and S.I.Zavyalov

It is known [1,2] that the reaction between cyclic ketones and 1-acetyl-cyclohexene or 1-acetyl-1-cyclopentene can proceed with formation of derivatives of decahydrophenanthrene (I) or octahydrobenzindan (II).

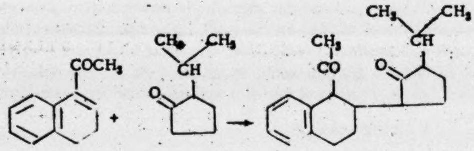


These reactions take place in two stages: first the saturated ketone under the influence of the alkaline catalyst adds at the double bond of the acetylcyclohexene or acetylcyclopentene according to a Michael type of reaction, and then the diketone formed cyclizes by means of an intramolecular crotonic condensation.

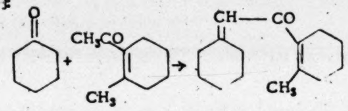
This method of building up polycyclic systems has been successfully applied to the synthesis of several polycyclic compounds related to steroids. Thus, from α-tetralone (3,4-dihydro-1(2H)-naphthalenone) and from 6-methoxy-α-tetralone it has been found possible to pass to compounds related in structure to estrone [1,2]:



In certain cases, when there is some obstacle in the way a Michael or crotonic condensation, the reaction between the cyclic ketone and 1-acetyl-1-cyclohexene stops at one of the stages and does not therefore lead to a polycyclic system. One such example is the reaction between 2-isopropyl-1-cyclopentanone and 1-acetyl-3,4-dihydronaphthalene [3]:

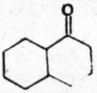


Here cyclization does not occur because of the blocking action of the isopropyl group on the keto group. It is true that under more severe conditions it has been possible to effect cyclodehydration by a special method also in this case. The reaction between cyclic ketones and derivatives of 1-acetyl-1-cyclohexene that are substituted in the 2-position is of particular interest [4,5]:

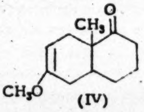


In this case the Michael addition reaction is inhibited and only the crotonic condensation is therefore possible.

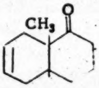
In the present work we have investigated the reaction with 1-acetyl-1-cyclohexene of certain bicyclic ketones in an attempt to prepare substances related in structure to hormones of the androstane series. As bicyclic ketones we have used 1-decalone (octahydro-1(2H)-naphthalenone) (III), the 6-methoxy-8a-methyl derivative of 1-octalone (3,4,4a,5,8,8a-hexahydro-1(2H)-naphthalenone) (IV), 8a-methyl-1-octalone (V), and 3a,4,7,7a-tetrahydro-3,7a-dimethyl-1-indanone (VI):



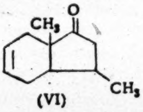
(III)



(IV)

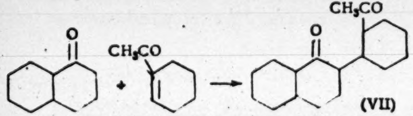


(V)

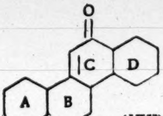


(VI)

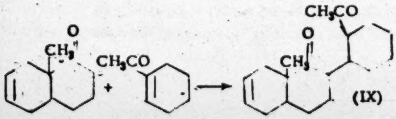
These were converted by the aid of sodamide in ethereal solution into sodium derivatives, which were then submitted to the action of 1-acetyl-1-cyclohexene. In the case of 6-methoxy-8a-methyl-1-octalone (IV) we did not observe appreciable interaction, and the substances taken for reaction were recovered unchanged. In the remaining cases, high-boiling products were isolated in yields of 35-40%; in elementary composition they corresponded not to the tetracyclic ketones VIII, X and XII, but to the compounds VII, IX, and XI, formed as a result of the Michael condensation; these have a ruptured C ring (the difference between the two types of substance in carbon content is about 5%).



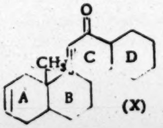
(VII)



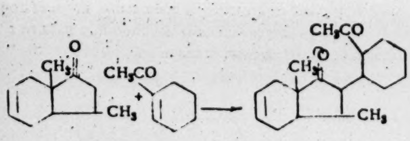
(VIII)



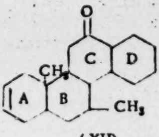
(IX)



(X)



(XI)



(XII)

The product of the reaction of 1-decalone with 1-acetyl-1-cyclohexene did not undergo hydrogenation in methanol solution in presence of a Pt catalyst, but treatment with excess of 2,4-dinitrophenylhydrazine gave the bis(2,4-dinitrophenylhydrazone). The reaction product from tetrahydro-3,7a-dimethyl-1-indanone and 1-acetyl-1-cyclohexene absorbed 1 molecular proportion of hydrogen at a Pt catalyst. Thus, under normal conditions intramolecular crotonic condensation of compounds VII, IX, and XI does not occur. The obstacle to this reaction is evidently the steric hindrance that is known to occur; it renders the keto group in ring B passive.

EXPERIMENTAL

1-Acetyl-1-cyclohexene (b.p. 85-87° at 15 mm; n_D^{20} 1.4900) was prepared by the condensation of acetyl chloride with cyclohexene in presence of stannic chloride and subsequent treatment of the reaction product with diethylaniline [6].

6-Methoxy-8a-methyl-1-octalone (IV) (b.p. 88-89° at 0.1 mm; n_D^{20} 1.5089) was prepared by the action of 2-methoxybutadiene on 2-methyl-2-cyclohexen-1-one [7].

cis-1-Decalone (III) (b.p. 113-114° at 15 mm; n_D^{20} 1.4900) was prepared by the oxidation of decahydro-1-naphthol [8].

Tetrahydro-3,7a-dimethyl-1-indanone (VI) (b.p. 90-92° at 7 mm; n_D^{23} 1.4875) was prepared by the condensation of butadiene with 2,4-dimethyl-2-cyclopenten-1-one [9].

8a-Methyl-1-octalone (V) (b.p. 70-73° at 3 mm; n_D^{20} 1.5042) was prepared by the action of butadiene on 2-methyl-2-cyclohexen-1-one [10].

The Reaction of 1-Decalone with 1-Acetyl-1-cyclohexene

A solution of 1-decalone (3 g; 1 mol) in dry ether (50 ml) and finely ground sodamide (0.8 g; 1 mol) were vigorously mixed together at room temperature for 7 hrs, a stream of dry hydrogen being passed through the reaction mixture. The solution was boiled on the water bath for 1 hr to remove residual ammonia. The suspension was cooled with ice, and 1-acetyl-cyclohexene (2.4 g; 1 mol) was added dropwise with stirring. Stirring with cooling was continued for a further 2 hrs. The mixture was then allowed to stand at room temperature overnight. Before further treatment, the reaction mixture was boiled on the water bath for 1½ hrs; the solution was then cooled with ice and treated with hydrochloric acid (diluted 1:1) until weakly acid to Congo red. The ether layer was separated and dried with sodium sulfate. The ether was driven off, and the residue was vacuum-distilled. The reaction product VII (1.9 g) was obtained; b.p. 172-178° at 2 mm.

Found %: C 78.07; 78.49; H 10.26; 10.10
$C_{18}H_{28}O_2$. Calculated %: C 78.26; H 10.15

The substance did not hydrogenate in methanol solution in presence of a Pt catalyst, but it reacted with excess of 2,4-dinitrophenylhydrazine to give the bis(2,4-dinitrophenylhydrazone), which melted with decomposition at 213-215° (from benzene).

Found %: N 17.79; 17.83
$C_{30}H_{36}O_8N_8$. Calculated %: N 17.61

The Reaction of 8a-Methyl-1-octalone with 1-Acetyl-1-cyclohexene

8a-Methyl-1-octalone (V) (2 g; 1 mol) in dry ether (40 ml), finely ground sodamide (0.5 g; 1 mol), and 1-acetyl-1-cyclohexene (1.5 g; 1 mol) were taken for reaction. The reaction product (1.2 g) was IX, b.p. 153-157° at 0.05 mm; n_D^{20} 1.5412.

Found %: C 78.87; 78.84; H 10.08; 10.02
$C_{19}H_{28}O_2$. Calculated %: C 79.16; H 9.73

The 2,4-dinitrophenylhydrazone melts at 215-217° with decomposition (from benzene):

Found %: N 11.84; 11.77
$C_{25}H_{32}O_5N_4$. Calculated %: N 11.9

Reaction of 3a, 4, 7, 7a-tetrahydro-3, 7a-dimethyl-1-indanone with 1-Acetyl-1-cyclohexene

3a,4,7,7a-tetrahydro-3,7a-dimethyl-1-indanone (VI) (3 g; 1 mol.) in dry ether (50 ml), finely ground sodamide

(0.72 g; 1 mol), and 1-acetyl-1-cyclohexene (2.2 g; 1 mol) were taken for reaction. The experiment was carried out as described above. The reaction product (2.2 g) was XI, b.p. 166-170° at 2 mm; n_D^{20} 1.5395.

Found %: C 78.80; 78.89; H 9.51; 9.43
$C_{19}H_{28}O_2$. Calculated %: C 79.16 H 9.73

The 2,4-dinitrophenylhydrazone melts at 223-224° with decomposition (from benzene):

Found %: N 12.2; 11.98
$C_{25}H_{32}O_5N_4$. Calculated %: N 11.9

On hydrogenation in methanol solution at a Pt catalyst the substance absorbs 1 mol of hydrogen.

Attempt to Condense 6-Methoxy-8a-methyl-1-octalone with 1-Acetyl-1-cyclohexene

A solution of the sodium derivative of 6-methoxy-8a-methyl-1-octalone, prepared from the ketone (IV) (3 g; 1 mol), finely ground sodamide (0.6 g; 1 mol), and dry ether (50 ml), was treated with 1-acetyl-1-cyclohexene (1.9 g; 1 mol) under the conditions described above. The original substances and some resinous products (0.4 g) were isolated from the reaction mixture.

SUMMARY

The condensation has been carried out of 1-decalone (III), 8a-methyl-1-octalone (V), and 3a,4,7,7a-tetrahydro-3,7a-dimethyl-1-indanone (VI) with 1-acetyl-1-cyclohexene. The products were the polycyclic diketones VII, IX, and XI, which under the conditions of the experiment did not undergo a further intramolecular crotonic condensation.

Received January 28, 1952

Institute of Organic Chemistry of the
USSR Academy of Sciences

LITERATURE CITED

[1] W. Rapson and R. Robinson, J. Chem. Soc. 1285 (1935).

[2] R. Robinson and coworkers, J. Chem. Soc. 752, 757, 763 (1936).

[3] A. Birch and R. Robinson, J. Chem. Soc. 503 (1944).

[4] W. Johnson, J. Szmuszkovicz and M. Miller, J. Am. Chem. Soc. 72, 3726 (1950).

[5] R. Turner and D. Voitle, J. Am. Chem. Soc. 72, 4166 (1950).

[6] G. Darzens, Comptes rend. 150, 709 (1910).

[7] I. N. Nazarov and L. D. Bergelson, J. Gen. Chem. 20, 654 (1950).*

[8] V. I. Nikitin, J. Gen. Chem. 15, 403 (1945).

[9] I. N. Nazarov and L. I. Shmonina. J. Gen. Chem. 20, 880 (1950).**

[10] W. Nudenberg, L. Butz, J. Am. Chem. Soc. 65, 1436 (1943).

---

*See Consultants Bureau translation, p. 685.

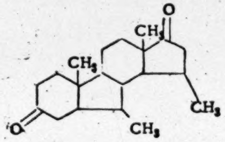
** See Consultants Bureau translation, p. 911.

ACETYLENE DERIVATIVES

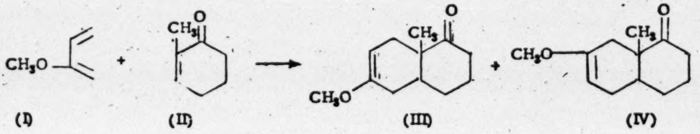
COMMUNICATION 126. SYNTHESIS OF POLYCYCLIC COMPOUNDS RELATED TO STEROIDS. XIV. SYNTHESIS OF TETRACYCLIC KETONES HAVING A METHYLCYCLOPENTANE B RING

I. N. Nazarov, V. F. Kucherov, and L. N. Terekhova

As already shown [1], it is possible to proceed from 2,4-dimethyl-2-cyclopenten-1-one (V) by means of diene condensations and via the intermediate compounds VI, VIII, and X to the synthesis of a tetracycloketone, which has a β-norandrostane skeleton and was provisionally assigned the structure of a normal steroid ketone:

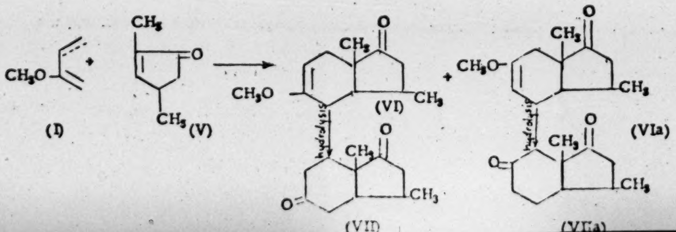


However, subsequent detailed study of the diene synthesis has shown that condensation of 2-methoxybutadiene with unsaturated cyclic ketones such as 2-methyl-2-cyclohexen-1-one leads to a mixture of para and meta condensation products, with predominant formation of the normal addition product, which has the methoxy group in the para-position to the angular methyl group. In this work the example was taken of the condensation of 2-methoxybutadiene (I) with 2-methyl-2-cyclohexen-1-one (II), and it was shown that the main liquid product of the diene condensation, which has a narrow boiling range and a constant refractive index, contains, in addition to the main product of normal condensation cis-6-methoxy-8a-methyl-1-octalone (cis-3,4,4a,5,8,8a-hexahydro-6-methoxy-8a-methyl-1(2H)-naphthalenone) (III), about 5% of the meta isomer (IV):



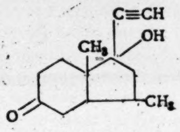
The meta isomer (IV) that was formed could not be isolated by fractional distillation, and its presence and structure were demonstrated after its conversion into the corresponding crystalline acetylenic hydroxy ketones. The condensation of 2-methoxybutadiene (I) with 2,4-dimethyl-2-cyclopenten-1-one (V) proceeds in similar fashion, and this forms the subject of the present communication.

2-Methoxybutadiene (I) heated with a 25-30-fold excess of 2-4-dimethyl-2-cyclopenten-1-one (V) at 230° for 1.5 hr and then carefully distilled under reduced pressure yields cis-3a,4,7,7a-tetrahydro-5-methoxy-3,7a-dimethyl-1-indanone (VI), b.p. 103-104° at 1.5 mm and n_D^{20} 1.4960, in 25-30% yield. However, the product obtained is not an individual compound, and after hydrolysis into the corresponding diketone (VII) a mixture of disemicarbazones can be made and separated by crystallization:

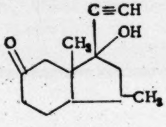


Condensation of the methoxytetrahydroindanone (VI) (b.p. 103-104° 1.5 mm; n_D^{20} 1.4960) with acetylene in liquid ammonia in presence of metallic potassium and subsequent acid hydrolysis of the product gave a 25% yield of a crystalline acetylenic compound (VIII), m.p. 135-136°, which has been described previously [1]. From the liquid portion formed in the acetylene synthesis it was found possible by fractional distillation and treatment with ether and with petroleum ether (see Experimental part) to isolate another similar product (IX), m.p. 118-119.5° and giving a semicarbazone m.p. 200-201°, in 6% yield.

According to the results obtained in our laboratory on the condensation of 2-methoxybutadiene and 2-methyl-2-cyclohexen-1-one, the main acetylenic product, m.p. 135-136°, will be 1-ethynyltetrahydro-1-hydroxy-3,7a-dimethyl-1-5(4H)-indanone (VIII), and the other isomer, which is formed in small amount, will be 1-ethynyl-tetrahydro-1-hydroxy-3,7a-dimethyl-6(5H)-indanone (IX):

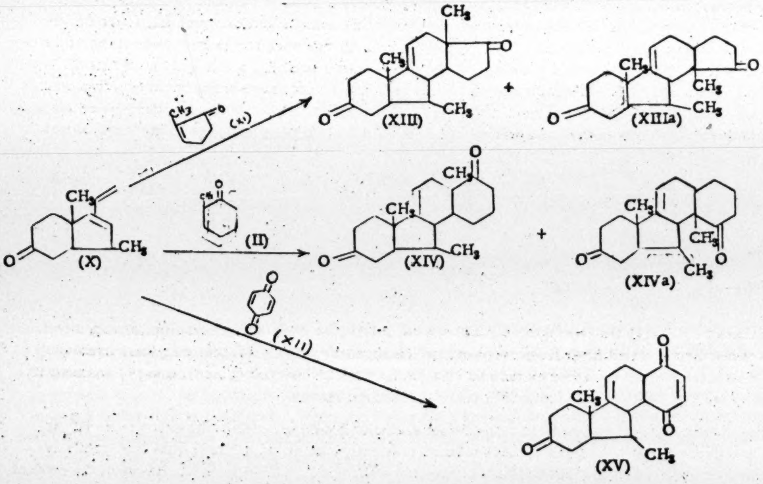


(VIII)



(IX)

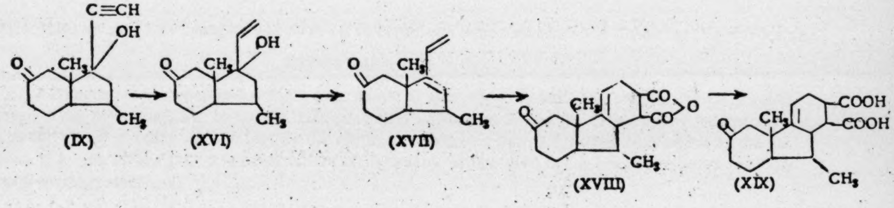
The main product (VIII) is converted by selective hydrogenation over a Pd catalyst and subsequent dehydration into the previously described 3a, 4,7,7a-tetrahydro-1,3a-dimethyl-3-vinyl-6(5H)-indenone (X), which on condensation with 2-methyl-2-cyclopenten-1-one (XI) or with 2-methyl-2-cyclohexen-1-one (II) yields in 60% yield the tetracyclic ketone XIII or XIV respectively, in the form of a viscous glasslike product which is a mixture of two possible structural forms (XIII and XIIIa; XIV and XIVa).



Condensation of the vinyltetrahydroindenone (X) with p-quinone (XII) gives a high yield of the individual substance (XV) which on hydrogenation over a Pt catalyst absorbs about 3 moles of hydrogen.

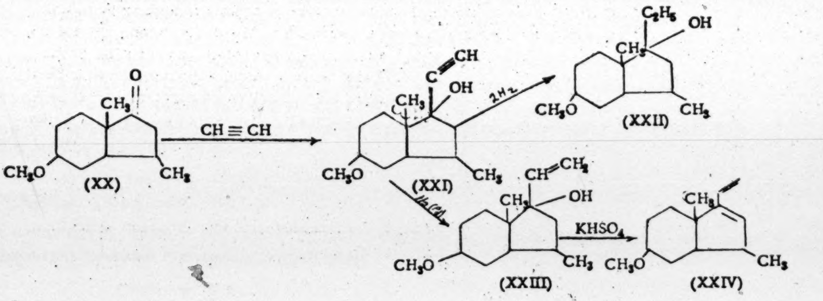
The isomeric acetylenic hydroxy ketone (IX) gives, on selective hydrogenation over a Pd catalyst, the corresponding tetrahydro-1-hydroxy-3,7a-dimethyl-1-vinyl-6(5H)-indanone (XVI) (m.p. 88-89°; semicarbazone, m.p. 166-167.5°), which on dehydration over potassium hydrogen sulfate yields 3,6,7,7a-tetrahydro-1,3a-dimethyl-3-vinyl-5(4H)-indenone (XVII), characterized as its crystalline semicarbazone, m.p. 187-188°. On condensation with maleic anhydride, the vinyltetrahydroindenone (XVII) gives the tricyclic fluorenedicarboxylic anhydride (XVIII), from which on hydrolysis is obtained the corresponding decahydro-4b, 9-dimethyl-6-oxofluorene-1,2-dicarboxylic acid (XIX):

BLANK
PAGE

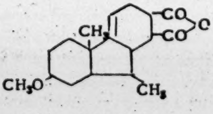

C≡CH
OH
O
CH₃
CH₃
(IX)
OH
O
CH₃
CH₃
(XVI)
O
CH₃
CH₃
(XVII)
CO
O
CO
CH₃
O
CH₃
(XVIII)
COOH
COOH
CH₃
O
CH₃
(XIX)

When the main methoxytetrahydroindanone (VI) is hydrogenated in alcohol at room temperature over a Pd catalyst, about 80% of the required amount of hydrogen is absorbed, and a non-homogeneous reaction product is obtained: 80-108° at 2 mm; n_D^{20} 1.4760-1.4820•. After careful fractionation, the main hydrogenation product, b.p. 94-98° at 2 mm; n_D^{20} 1.4785, may be isolated in about 60% yield; this has been described previously [1], and it corresponds in composition to hexahydro-5-methoxy-3,7a-dimethyl-1-indanone (XX), but is not an individual substance. When it is condensed with acetylene in liquid ammonia in presence of metallic potassium, a crystalline acetylenic methoxy alcohol, m.p. 114-115°, is obtained in about 35% yield; in accordance with our previous results, this compound has the structure 1-ethynylhexahydro-5-methoxy-3,7a-dimethyl-1-indanol (XXI). The other isomeric acetylenic alcohol could not be isolated.

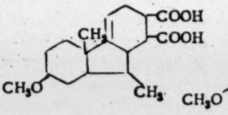
When the acetylenic methoxy alcohol(XXI)was exhaustively hydrogenated, 2 moles of hydrogen were absorbed, and the ethylmethoxy alcohol(XXII) was obtained. Selective hydrogenation of the acetylenic methoxyhexahydroindanol(XXI)over a Pd catalyst yielded a liquid vinyl compound (XXIII), which gave by dehydration over potassium hydrogen sulfate 3a,4,5,6,7,7a-hexahydro-6-methoxy-1,3a-dimethyl-3-vinylindene (XXIV) in good yield.


O
CH₃
CH₃O
CH₃
(XX)
CH ≡ CH
CH
C
OH
CH₃
CH₃O
CH₃
(XXI)
2H₂
C₂H₅
OH
CH₃
CH₃O
CH₃
(XXII)
H₂ (Pd)
CH=CH₂
OH
CH₃
CH₃O
CH₃
(XXIII)
KHSO₄
CH₃
CH₃O
CH₃
(XXIV)

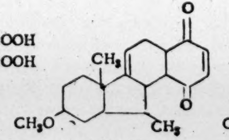
On condensation with maleic anhydride, the diere(XXIV)gives with 40% yield the tricyclic methoxyfluorenedicarboxylic anhydride(XXV) which yields on hydrolysis the corresponding 1,2,3,4b,5,6,7,8,8a,9a-decahydro-7-methoxy-4b, 9-dimethylfluorene-1,2-dicarboxylic acid (XXVI). The diene(XXIV) condenses with p-quinone to give the crystalline tetracyclic product(XXVII,)which does not undergo hydrogenation over a Pd catalyst under normal conditions. When the diene(XXIV)is condensed with 2-methyl-2-cyclohexen-1-one (II), the corresponding tetracyclic product (XXVIII) is formed as a viscous glasslike mass, which appears to be a mixture of the two possible structural isomers:


CO
O
CO
CH₃
CH₃O
CH₃

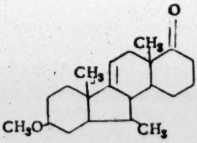
(XXV)


COOH
COOH
CH₃
CH₃O
CH₃

(XXVI)


O
CH₃
O
CH₃O
CH₃

(XXVII)


O
CH₃
CH₃
CH₃O
CH₃

(XXVIII)

• When more severe hydrogenation conditions are used (with heating and under a hydrogen pressure of 100 atm), partial hydrogenation of the carbonyl group occurs.

The tetracyclic ketones (XXVII) and (XXVIII) do not give crystalline semicarbazones and 2,4-dinitrophenylhydrazones.

EXPERIMENTAL

2,4-Dimethyl-2-cyclopenten-1-one (V) (b.p. 53-55° at 10 mm; n_D^{20} 1.4655) was prepared by the method developed in our laboratory, i.e. by the cyclization of allyl isopropenyl ketone [2]. 2-Methoxy-1,3-butadiene [1] (b.p. 75-76°; n_D^{20} 1.4435) was obtained by the splitting of methanol from 1,3,3-trimethoxybutane by the aid of sodium hydrogen sulfate [3]. The conditions of this synthesis, as improved in our laboratory, result in a 75% yield of 2-methoxybutadiene.

I. Condensation of 2-Methoxy-1,3 -butadiene with 2,4-Dimethyl-2-cyclopenten-1-one

A mixture of 2,4-dimethyl-2-cyclopenten-1-one (550 g), 2-methoxybutadiene (20 g), and pyrogallol (2 g) was heated in a steel autoclave at 230° for 1¼ hr. The mixture was cooled rapidly, more 2-methoxybutadiene (20 g) was added, and the mixture was again heated at 230° for 1¼ hr. The reaction product after vacuum fractionation yielded 410 g of the original 2,4-dimethyl-2-cyclopenten-1-one (n_D^{20} 1.4650), 95 g of the isomeric 2,4-dimethyl-4-cyclopenten-1-one (n_D^{20} 1.4735) and 38 g of a condensation product having b.p. 95-140° at 2 mm (n_D^{20} 1.4965).

From 208 g of condensation product obtained in different experiments there was isolated, after fractionating twice through a column, 100 g of 3a, 4,7,7a-tetrahydro-5-methoxy-3,7a-dimethyl-1-indanone (VI) [1], b.p. 103-104° at 1.5 mm; n_D^{20} 1.4960. It could not be purified further by repeated distillation.

II. Hydrolysis of 3a,4,7,7a-Tetrahydro-5-methoxy-3,7a-dimethyl-1-indanone

The methoxytetrahydroindanone(VI)(20 g) was stirred vigorously at room temperature with 3% hydrochloric acid (60 ml) for 5 hrs. The mixture was neutralized with potassium carbonate, saturated with ammonium chloride, and carefully extracted with ether. The ether extract was dried with sodium sulfate, the ether driven off, and the residue vacuum-distilled through a column. From the mixture of hydrolysis products there was separated, after three successive distillations, 6.5 g of a substance having b.p. 119-121° at 2 mm; n_D^{20} 1.4925, and corresponding to the previously described tetrahydro-3,7a-dimethyl-1,5(4H)-indandione (VII) [1]. From this diketone (1.1 g) the disemicarbazone (1 g), m.p. 210-217° with decomposition, was obtained by the usual method. After being boiled with 20 times its amount of methanol, the undissolved substance melted at 240-245° (dec.). By recrystallization from a large volume of methanol, this disemicarbazone was obtained in the form of fine needles, m.p. 253-254° (dec.).

Found %: N 28.18
$C_{13}H_{22}O_2N_3$. Calculated %: N 28.40

A second disemicarbazone was isolated by evaporating down the methanol mother liquor. After being recrystallized from methanol it melted at 224-225° (dec).

Found %: N 28.10
$C_{13}H_{23}O_2N_3$. Calculated %: N 28.40

A mixed test of these two disemicarbazones gave a m.p. of 234-236° (dec).

III. Condensation of 3a,4,7,7a-Tetrahydro-5-methoxy-3,7a-dimethyl-1-indanone (VI) with Acetylene

Liquid ammonia (350 ml) was poured into a three-necked flask, provided with a stirrer, dropping funnel, reflux condenser, and tube for the passage of acetylene, and cooled to −70° by means of a mixture of solid carbon dioxide and acetone. Metallic potassium (50 g) was added slowly. Dry acetylene (300 liter) was then passed over a period of 2 hrs, and at −70° a solution of 3a,4,7,7a-tetrahydro-5-methoxy-3,7a-dimethyl-1-indanone (VI, 100 g) in absolute ether (200 ml) was added over 1.5 hr. The mixture was stirred by passage of a feeble stream of acetylene for 4 hrs, and was left overnight at −70°. On the next day it was stirred for a further 10 hrs at this temperature, and on the following day the ammonia was evaporated off. The residue was decomposed at −10° by addition of dry ammonium chloride (100 g); a further addition of ether (200 ml) was made, and water was added until the precipitate dissolved. The ether layer was separated, and the water layer extracted twice with ether. The united ether extracts were washed with a small amount of water, and the ether was driven off.

A 2% solution of hydrochloric acid (100 ml) was added to the residue, and the mixture was stirred vigorously at room temperature for 5 hrs. The crystalline product that was precipitated was filtered off and washed with 30% methanol. A substance (21.5 g) m.p. 134-136°, identical with the previously described acetylenic hydroxy ketone (VIII) [1] was obtained. The liquid product was extracted with ether, and the ether extract was washed with bicarbonate solution and dried. The residue remaining after driving off the ether was vacuum-distilled at 0.02 mm. The following fractions were obtained:

Fraction 1, b.p. 75-100°; n_D^{20} 1.4960; 15 g;

Fraction 2, b.p.100-110°; n_D^{20} 1.4995; 5 g;

Fraction 3, b.p.110-125°; n_D^{20} 1.5070; 52.5 g.

After addition of a small amount of absolute ether, fraction 3 gradually began to crystallize. After 5 days, the crystals that had separated were filtered off and washed with absolute ether. A further 4.8 g of the acetylenic hydroxy ketone, m.p. 134-136°, was obtained. The total yield of the acetylenic hydroxy ketone (VIII)(1-ethynyltetrahydro-1-hydroxy-3,7a-dimethyl-5(4H)-indanone)was 26.3 g (25% of theoretical).

From the ethereal solution, after addition of a small amount of petroleum ether and cooling, fine needle-like crystals separated and were filtered off after 5 days. 3 g of a substance melting at 110-114° was obtained. After removal of the solvents by distillation and vacuum fractionation of the residue, a fraction (29 g) was isolated having b.p. 145-150° at 2 mm; n_D^{20} 1.5090, from which by treatment with a mixture of petroleum ether and ethyl ether (1:1), with cooling and prolonged standing (10-15 days), a further 3.2 g of substance, m.p. 108-112°, was isolated.

The total yield of the second crystalline product was 6.2 g (5.8%), and after crystallization from acetone it had the constant m.p. 118-119.5°. Analysis showed the product to have a composition corresponding to 1-ethynyltetrahydro-1-hydroxy-3,7a-dimethyl-5(4H)-indanone (IX).

Found %: C 75.90; 75.90; H 8.83; 8.67
$C_{13}H_{18}O_2$. Calculated %: C 75.70; H 8.80

It was not found possible to isolate other individual products of the acetylene synthesis.

IV. Condensation of 3a,4,7,7a-Tetrahydro-1,3a-dimethyl-3-vinyl-6(5H)-indenone (X) with 2-Methyl-2-cyclopenten-1-one (XI)

A mixture of the diene(X)(1.4 g) (98-100° at 3 mm; n_D^{20} 1.5048), which has been described previously [1] and was prepared from the acetylenic alcohol(VIII,)2-methyl-2-cyclopenten-1-one(XI, 16.4 g) (b.p. 52-53° at 15 mm; n_D^{20} 1.4770) and pyrogallol (0.1 g) was heated at 170° in a glass ampoule for 5 hrs. Vacuum distillation yielded 2-methyl-2-cyclopenten-1-one (14.7 g), the original diene (X) (0.9 g) and the tetracyclic diketone(XIII)(1 g) as a thick pale-yellow liquid, b.p. 170-180° at 0.02 mm; n_D^{20} 1.5370.

Found %: C 79.75; 79.92; H 9.14; 9.13
$C_{19}H_{26}O_2$. Calculated %: C 79.70; " . H 9.10

The disemicarbazone of the tetracyclic diketone(XIII)melted after recrystallization from alcohol at 201-202° (dec).

Found %: N 20.90; 21.17
$C_{21}H_{32}O_2N_6$. Calculated %: N 21.0

When the tetracyclic diketone(XIII)was hydrogenated in alcohol over a Pt catalyst, 1 molecular equivalent of hydrogen was absorbed, and the hydrogenation product was separated as a colorless glass-like substance, b.p. 130-140° at 0.012 mm; n_D^{20} 1.5320.

Found %: C 79.16; 78.97; H 10.08; 10.10
$C_{19}H_{28}O_2$. Calculated %: C 79.16; H 9.73

V. Condensation of 3a,4,7,7a-Tetrahydro-1,3a-dimethyl-3-vinyl-6(5H)-indenone (X) with 2-Methyl-2-cyclohexen-1-one (II)

A mixture of the diene (X) (1.6 g), 2-methyl-2-cyclohexen-1-one (II, 22.5 g) (b.p. 65-67° at 16 mm; n_D^{20} 1.4810), and pyrogallol (0.1 g) was heated at 170° in a glass ampoule for 5 hrs. Vacuum distillation yielded 2-methyl-2-cyclohexen-1-one (21 g), the original diene (X) (1.1 g), and the tetracyclic diketone(XIV)(0.68 g) as a viscous liquid, b.p. 143-150° at 0.013 mm; n_D^{20} 1.5375.

Found %: C 79.95; 80.20; H 9.20; 9.24;

$C_{20}H_{28}O_2$. Calculated %: C 80.00 H 9.30

When the tetracyclic diketone (XIV) was hydrogenated in alcohol over a Pt catalyst, 2 molecular equivalents of hydrogen was absorbed, and the hydrogenation product was obtained as a colorless viscous liquid, b.p. 150-160° at 0.02 mm; n_D^{20} 1.5330.

Found %: C 78.70; 78.66; H 10.24; 10.20

$C_{20}H_{32}O_2$. Calculated %: C 78.95; H 10.53

VI. Condensation of 3a,4,7,7a-Tetrahydro-1,3a-dimethyl-3-vinyl-6(5H)-indenone (X) with p-Quinone (XII)

The diene (X) (2 g), p-quinone (1.05 g), and pyrogallol (0.05 g) were dissolved in absolute dioxane (15 ml) and heated at 60° for 5 hrs. The dioxane was driven off, and a crystalline product (1.8 g) of m.p. 134-139° was obtained. Crystallization from methanol yielded the pure tetracyclic triketone (XV) m.p. 136-137°.

Found %: C 76.88; 76.61; H 7.51; 7.48

$C_{19}H_{22}O_3$. Calculated %: C 76.51; H 7.38

With semicarbazide the tetracyclic triketone (XV) gave a disemicarbazone that did not melt below 300°. It was purified by reprecipitation by water from methanol solution.

Found %: N 19.90; 20.09

$C_{21}H_{28}O_3N_6$. Calculated %: N 20.38

VII. Selective Hydrogenation of 1-Ethynyltetrahydro-1-hydroxy-3,7a-dimethyl-6(5H)-indanone (IX)

The acetylenic hydroxytetrahydroindanone (IX) (2.55 g), m.p. 117-118°, was dissolved in absolute dioxane (10 ml) and hydrogenated over a Pd catalyst at 22° and 742 mm. When 310 ml of hydrogen had been absorbed (305 ml would be required for one double bond), the catalyst was filtered off, and the dioxane driven off under reduced pressure. The crystalline product was mixed with petroleum ether and then filtered off. 2.25 g of a substance melting at 84-86° was obtained. After crystallization from petroleum ether, tetrahydro-1-hydroxy-3,7a-dimethyl-1-vinyl-6(5H)-indanone (XVI) had m.p. 88-89°.

Found %: C 75.50; 75.30; H 9.71; 9.67

$C_{13}H_{20}O_2$. Calculated %: C 75.20; H 9.62

The semicarbazone was obtained after crystallization from 40% methanol as fine needles, m.p. 166-167.5°.

Found %: N 15.51; 15.77

$C_{14}H_{23}O_2N_3$. Calculated %: N 15.83

VIII. Dehydration of Tetrahydro-1-hydroxy-3,7a-dimethyl-1-vinyl-6(5H)-indanone (XVI)

A mixture of the vinylhydroxy ketone (XVI) (1.7 g) and finely ground anhydrous potassium hydrogen sulfate (0.8 g) was heated in a Claisen flask at 120° under a pressure of 80 mm for 20 min. The dehydration product was extracted with ether, the ethereal solution dried over anhydrous magnesium sulfate, and the ether driven off. By distillation under reduced pressure, the residue yielded 3a,6,7,7a-tetrahydro-1,3a-dimethyl-3-vinyl-5(4H)-indenone (XVII), b.p. 125-130° at 7 mm; n_D^{20} 1.5160. The diene (XVII) rapidly turned yellow on standing, becoming a thick yellow mass. It was characterized as its crystalline semicarbazone, which after crystallization from 80% methanol melted at 187-188°.

Found %: N 17.40

$C_{14}H_{21}ON_3$. Calculated %: N 17.08

IX. Condensation of 3a,6,7,7a-Tetrahydro-1,3a-dimethyl-3-vinyl-5(4H)-indenone (XVII) with Maleic Anhydride

A mixture of the diene XVII (0.55 g) and maleic anhydride (0.3 g) was heated in a glass ampoule at 120-125° for 3 hrs. After cooling and standing for a long time (20 days), the reaction product partially crystallized out. After treatment with a mixture of benzene and petroleum ether (1:1), the crystalline product was filtered off. The tricyclic fluorenedicarboxylic anhydride XVIII (0.25 g) was obtained; m.p. after crystallization from a mixture of benzene and petroleum ether: 206-207°.

Found %: C 70.89; 70.99; H 7.05; 7.02
$C_{17}H_{20}O_4$. Calculated %: C 70.83; H 6.94

The anhydride XVIII (0.1 g) was hydrolyzed by boiling it with 2% HCl (4 ml) until it was almost completely dissolved (3 hrs). The hot filtered solution gave, on cooling, a fine crystalline precipitate of m.p. 226-230°. After crystallization from 40% ethanol, 1,2,3,4b,5,6,7,8,8a,9a-decahydro-4b,9-dimethyl-6-oxofluorene-1,2-dicarboxylic acid (XIX) had m.p. 236-238° (dec).

Found %: C 65.91; 66.04; H 7.26; 7.45
$C_{17}H_{22}O_5$. Calculated %: C 66.45; H 7.20

X. Hydrogenation of 3a,3,7,7a-Tetrahydro-5-methoxy-3,7a-dimethyl-1-indanone (VI)

The methoxytetrahydroindanone VI (n_D^{20} 1.4960) (10 g) was dissolved in absolute dioxane (20 ml) and hydrogenated over a Pd catalyst at 20° and 738 mm. The amount of hydrogen absorbed (990 ml in 17 hrs) corresponded to 80% of the theoretical quantity. On addition of fresh catalyst, no further hydrogenation occurred. The catalyst was filtered off, the solvent driven off, and the liquid hydrogenation product vacuum-distilled. By a double distillation through a column, a substance (5.7 g, b.p. 94-98° at 2 mm, n_D^{20} 1.4785) was isolated which was found to be the previously described [1] hexahydro-5-methoxy-3,7a-dimethyl-1-indanone (XX).

XI. Condensation of Hexahydro-5-methoxy-3,7a-dimethyl-1-indanone with Acetylene

Liquid ammonia (250 ml) was poured into a three-necked flask cooled to −70° and provided with a stirrer, thermometer, dropping funnel, and tube for the passage of acetylene. Metallic potassium (14 g) was added slowly with stirring, and acetylene was then passed for 30 min (100 liter). A solution of hexahydro-5-methoxy-3,7a-dimethyl-1-indanone (XX) (25 g) in absolute ether (20 ml) was added slowly (over 1 hr). The mixture was stirred at −70° with passage of a feeble stream of acetylene for 5 hrs, and was then left overnight. On the next day stirring was continued for a further 10 hrs, and the mixture was again left overnight. The ammonia was evaporated off, and the reaction product was decomposed at not above 0° by addition of ammonium chloride (35 g); ether (100 ml) was added, and then water until the precipitate present was dissolved. The ether layer was separated, and the aqueous part was extracted twice with ether; the united ether extracts were washed with a small amount of cold water, and then dried over magnesium sulfate. After removal of the ether the residue crystallized out (on standing), giving a half-solid mass. The crystalline product was filtered off and washed with a small amount of cold ether. The acetylenic alcohol XXI (7.2 g, m.p. 111-113°) was obtained. The liquid reaction product was freed from solvent and vacuum-distilled. The following fractions were obtained:

Fraction 1, b.p. 75-110° at 1.5 mm; n_D^{22} 1.4820; 3 g

Fraction 2, b.p. 110-135° at 1.5 mm; n_D^{22} 1.4980; 10 g

By treatment of fraction 2 with petroleum ether and cooling of the solution obtained, a further 2.1 g of crystals m.p. 111-113° was obtained. The total yield of the crystalline product of the acetylene synthesis was 9.3 g, i.e. 33.5% of theoretical. After crystallization from petroleum ether the 1-ethynylhexahydro-5-methoxy-3,7a-dimethyl-1-indanol (XXI) obtained had m.p. 114-115°.

Found %: C 75.81; 75.76; H 10.22; 10.33
$C_{14}H_{22}O_2$. Calculated %: C 75.65; H 10.00

It was not found possible to separate other individual substances from the liquid product of the acetylene synthesis.

XII. Hydrogenation of 1-Ethynyl-hexahydro-5-methoxy-3,7a-dimethyl-1-indanol (XXI)

a) The acetylenic methoxyhexahydroindanol XXI (1.5 g) was exhaustively hydrogenated in dioxane solution over a Pd catalyst and yielded by distillation the ethylmethoxy alcohol XXII (1.2 g) having b.p. 116-117° at 2.5 mm; n_D^{20} 1.4870; d_4^{20} 0.9920; found MR_D 65.64; calculated MR_D for $C_{14}H_{26}O_2$ 65.62.

Found %: C 74.26; 74.05; H 11.75; 11.62
$C_{14}H_{26}O_2$. Calculated %: C 74.28; H 11.58

b) The acetylenic methoxyhexahydroindanol(XXI)(3.6 g) was dissolved in absolute dioxane (30 ml) and hydrogenated over a Pd catalyst at 22° and 748 mm. The hydrogenation was stopped when 415 ml of hydrogen had been absorbed (400 ml of H_2 is required for one double bond), the catalyst was filtered off, the dioxane was driven off, and the residue was vacuum-distilled. The product was hexahydro-5-methoxy-3,7a-dimethyl-1-vinyl-1-indanol (XXIII) (3.2 g) having b.p. 120-121° at 2.5 mm; n_D^{20} 1.4970; d_4^{20} 1.0118; found MR_D 64.88; calculated MR_D 65.15.

Found %: C 74.40; 74.60; H 11.10; 11.10
$C_{14}H_{24}O_2$. Calculated %: C 74.95; H 10.74

XIII. Dehydration of Hexahydro-5-methoxy-3,7a-dimethyl-1-vinyl-1-indanol (XXIII)

A mixture of the vinylmethoxyhexahydroindanol(XXIII)(4.6 g) and finely ground anhydrous potassium hydrogen sulfate (2.3 g) was heated in a Claisen flask at 120-130° under a pressure of 80 mm for 30 min. The water was driven off, and the dehydration product was vacuum-distilled yielding 3a,4,5,6,7,7a-hexahydro-6-methoxy-1,3a-dimethyl-3-vinylindene (XXIV) (3.3 g), b.p. 110-111° at 7 mm; n_D^{20} 1.4980. The diene obtained (XXIV) is extremely unstable, and it was used directly for further diene condensations.

XIV. Condensation of 3a,4,5,6,7,7a-Hexahydro-6-methoxy-1,3a-dimethyl-3-vinylindene (XXIV) with Maleic Anhydride

A mixture of the diene(XXIV)(0.9 g) and maleic anhydride (0.45 g) was heated in a glass ampoule at 120° for 2.5 hrs. After standing for 2 days, the reaction product partially crystallized out; the crystals were filtered off and washed with petroleum ether. After crystallization from petroleum ether containing a little benzene, the tricyclic fluorenecarboxylic anhydride(XXV)(0.4 g) was obtained as colorless needles m.p. 115-116°.

Found %: C 70.76; 70.96; H 8.21; 8.18
$C_{18}H_{24}O_4$. Calculated %: C 71.00; H 7.95

The anhydride(XXV)(0.25 g) was hydrolyzed by boiling for 3 hrs with 3% HCl (3 ml). After the solution had cooled, the crystalline product was filtered off and washed with water. After crystallization from 50% alcohol, 0.2 g was obtained of 1,2,3,4b,5,6,7,8,8a,9a-decahydro-7-methoxy-4b,9-dimethylfluorene-1,2-dicarboxylic acid (XXVI), m.p. 216-217°.

Found %: C 67.17; 67.22; H 8.46; 8.70
$C_{18}H_{26}O_5$. Calculated %: C 67.05; H 8.44

XV. Condensation of 3a,4,5,6,7,7a-Hexahydro-6-methoxy-1,3a-dimethyl-3-vinylindene (XXIV) with p-Quinone (XII)

The diene(XXIV)(0.8 g) and p-quinone (0.4 g) were dissolved in absolute dioxane (10 ml) and heated at 60-65° for 5 hrs. The viscous yellow reaction product that remained after removal of solvent was vacuum-distilled, and a substance (0.5 g) of b.p. 135-150° at 0.02 mm was obtained. Treatment with a small amount of cold alcohol gave the crystalline tetracyclic diketone(XXVII,)which after crystallization from 60% alcohol had m.p. 125-126°.

Found %: C 75.62; 75.70; H 8.15; 8.40
$C_{20}H_{26}O_3$. Calculated %: C 76.30; H 8.35

The tetracyclic diketone(XXVII)does not give crystalline derivatives with semicarbazide or with 2,4-dinitrophenylhydrazine and is not hydrogenated in presence of a Pd catalyst.

XVI. Condensation of 3a,4,5,6,7,7a-Hexahydro-6-methoxy-1,3a-dimethyl-3-vinylindene (XXIV) with 2-Methyl-2-cyclohexen-1-one (II)

The diene(XXIV)(1.1 g) was dissolved in 2-methyl-2-cyclohexen-1-one (15 g) and heated in a glass ampoule at 180° for 5 hrs. The products of distillation were 2-methyl-2-cyclohexen-1-one (13.2 g), the original diene (0.4 g) and the tetracyclic ketone(XXVIII)(0.62 g) as a light-yellow, glasslike liquid, b.p. 135-150° at 0.015 mm.

Found %: C 79.24; 79.27; H 10.50; 10.65
$C_{21}H_{32}O_2$. Calculated %: C 79.60; H 10.25

The tetracyclic ketone(XXVIII)does not give a crystalline semicarbazone or 2,4-dinitrophenylhydrazone.

SUMMARY

1. Heating of 2-methoxy-1,3-butadiene (I) with 2,4-dimethyl-2-cyclopenten-1-one (V) yields as the main product the methoxytetrahydroindanone (VI), but there is formed in small amount also the isomeric methoxytetrahydroindanone (VIa). On condensation of the mixture (VI + VIa) with acetylene in liquid ammonia and subsequent hydrolysis of the product, there are obtained two crystalline acetylenic hydroxy ketones, 1-ethynyltetrahydro-1-hydroxy-3,7a-dimethyl-5(4H)-indanone (VIII) and 1-ethynyltetrahydro-1-hydroxy-3,7a-dimethyl-6(5H)-indanone (IX). A number of derivatives were prepared from the latter – the vinylhydroxy ketone (XVI), the dienone (XVII), the anhydride (XVIII), and the keto acid (XIX).

2. By condensation of the previously described dienone X with 2-methyl-2-cyclopenten-1-one (XI), with 2-methyl-2-cyclohexen-1-one (II), and with p-quinone (XII), the steroid tetracyclic ketones (XIII, XIV, and XV) having a five-membered B ring have been prepared.

3. By condensation of hexahydro-5-methoxy-3,7a-dimethyl-1-indanone (XX) with acetylene in liquid ammonia, 1-ethynylhexahydro-5-methoxy-3,7a-dimethyl-1-indanol (XXI) was prepared, and from this there were obtained the compounds hexahydro-5-methoxy-3,7a-dimethyl-1-vinyl-1-indanol (XXIII) and 3a,4,5,6,7,7a-hexahydro-6-methoxy-1,3a-dimethyl-3-vinylindene (XXIV).

4. By condensation of the diene (XXIV) with maleic anhydride, with p-quinone, and with 2-methyl-2-cyclohexen-1-one there were obtained the tricyclic anhydride (XXV), the acid (XXVI), and the tetracyclic methoxy ketones (XXVII and XXVIII).

Received November 25, 1951

Institute of Organic Chemistry of the
USSR Academy of Sciences

LITERATURE CITED

[1] I. N. Nazarov, L. N. Terekhova, and L. D. Bergelson. J. Gen. Chem. 20, 662 (1950).*

[2] I. N. Nazarov and I. I. Zaretskaya. Bull. Acad. Sci. USSR. Div. Chem. Sci., 65 (1944).

[3] H. Dukstra, J. Am. Chem. Soc. 57, 2255 (1935).

---

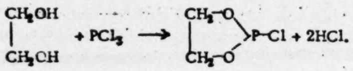
* See Consultants Bureau translation, p.697.

BLANK
PAGE

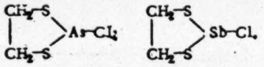
ETHYLENE ESTER OF PHOSPHOROCHLORIDODITHIOUS ACID, AND RELATED SUBSTANCES

A. E. Arbuzov and V. M. Zoroastrova

In previous papers we have studied the action of phosphorous trichloride on simple glycols in presence of pyridine or of dimethylaniline [1], e.g.:



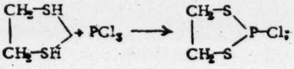
The chlorido ester obtained reacts with alcohols in presence of pyridine to give the corresponding mixed esters of phosphorous acid. In the literature there are described sulfur compounds of analogous structure containing an arsenic [2] or antimony [3] atom, which may be prepared by the action of arsenic trichloride or antimony trichloride on 1,2-ethanedithiol:



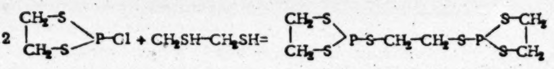
We have not been able to find any data concerning the synthesis of the phosphorous analog in the literature.

We considered it to be of interest in relation to the development of the study of the properties of mixed alkyl cyclic esters of phosphorous acid to synthesize the corresponding thio analogs and to compare their properties with those of the oxygen derivatives. By the action of phosphorus trichloride on ethanedithiol in dry ether we have isolated two reaction products — a liquid and a crystalline solid.

The liquid product was found to be the expected ethylene phosphorochloridodithioite (I), a colorless liquid that fumes strongly in air and has the following constants: b.p. 102-103°/10 mm; d_0^{20} 1.5297; n_D^{20} 1.6700; calculated MR_D 38.79; found MR_D 38.91. The solid product (II), m.p. 130°, was found to be the product of the action of three molecules of ethanedithiol on phosphorus trichloride, and resulted, evidently, from the action of ethanedithiol on the chlorido ester that had been formed:



(I)



(II)

The formation of an analogous product has been observed in the careful hydrolysis of the chlorido ester obtained by the action of 1,2-ethanedithiol on arsenic trichloride [2].

The chlorido ester I reacts with methanol in presence of pyridine with formation of a methyl ester (OCH_3 in place of Cl). Such alkyl cyclic esters may be prepared also by the action of Menshutkin acid chlorides on 1,2-ethanedithiol. Thus, by the action of ethyl phosphorodichloridite on ethanedithiol in presence of pyridine, the mixed ethyl ester was formed (OC_2H_5 in place of Cl).

Ethylene O-methyl phosphorodithioite is a liquid having the following constants: b.p. 97-98°/7.5 mm; d_4^{20} 1.3426; n_D^{20} 1.6200; calculated MR_D 40.30; found MR_D 40.33. The corresponding O-ethyl ester has the following constants: b.p. 98-99°/6 mm; d_0^{20} 1.2629; n_D^{20} 1.5922; calculated MR_D 44.90; found MR_D 45.09.

The cyclic thioesters obtained have the properties of tervalent phosphorus derivatives and give crystalline complex compounds with cuprous halides. They readily hydrolyze in air.

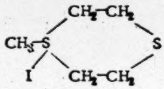
One of the most interesting properties of trialkyl esters of phosphorous acid is their conversion into quinquevalent phosphorous derivatives under the action of alkyl halides. In the case of alkyl cyclic esters of phosphorous acid, the conversion from tervalent to quinquevalent phosphorous may occur, as we have found previously, either with rupture of the cyclic system, or without rupture.

In the case of the thio-derivatives, the course of the reaction may be complicated, as was shown by Kabachnik, Divinsky, and Sidorenko [4], by the occurrence of the addition of alkyl halide not to phosphorous, but to sulfur, with subsequent splitting-off of a thioether and formation of the corresponding phosphorous halide derivative. The experiments that we have performed on the action of ethyl iodide on O-ethyl ethylene phosphorodithioite and on the action of triphenylmethyl bromide on ethylene O-methyl phosphorodithioite have shown that the reaction is complex, and we have not yet succeeded in sorting out the reaction products.

By the action of ethyl iodide on O-ethyl ethylene phosphorodithioite at 80-90° we obtained:

1) A product, b.p. 172-174°/4 mm, corresponding according to analysis to an isomerization product. However, the very high boiling point of the substance compels us to refrain from ascribing to it any definite structure, as an isomer of ethylene hydrogen phosphite.

2) A crystalline substance, m.p. 111-112°, which was found to be p-dithiane, confirmed by conversion into the monomethiodide:



m.p. 173-175°

3) The main bulk of reaction product, which was a transparent semisolid undistillable mass.

On hydrolysis of the substance of b.p. 172-174°/4 mm with 15% HCl at 170°, dithiane, m.p. 111°, and a liquid product, acid in nature and giving a barium salt, were isolated. The hydrolysis was accompanied by the separation of hydrogen sulfide. The action of methyl iodide on ethylene O-methyl phosphorodithioite in a sealed tube at 90° resulted, when the tube was opened, in a violent explosion. When the O-methyl or O-ethyl compounds were treated with triphenylmethyl bromide, the same crystalline product, m.p. 221-222°, was isolated in both cases. In its analysis it corresponds closely to the product that would be formed by addition of triphenylmethyl bromide to the phosphorous ester and subsequent splitting-off of methyl or ethyl bromide. However, hydrolysis of the product by means of hydrochloric acid did not yield triphenylmethylphosphonic acid, which would have indicated addition of triphenylmethyl bromide at phosphorous; nor did it give triphenylmethanol or triphenylmethanethiol, which might have been formed if the initial addition of triphenylmethyl bromide had occurred at sulfur. It was found possible to isolate only triphenylmethane from the reaction products.

Formation of triphenylmethane was observed by A. E. Arbuzov and B. A. Arbuzov [5] in the hydrolysis of Boyd's acid chloride with hydrochloric acid in sealed tubes in presence of ethanol. Separate experiments showed that formation of triphenylmethanol preceded formation of triphenylmethane. We have shown by specially designed experiments that under the conditions of the hydrolysis by hydrochloric acid of the product formed by the action of triphenylmethyl bromide on O-alkyl ethylene phosphorodithioite, i.e. in presence of the hydrogen sulfide formed in this reaction, triphenylmethanol is reduced to triphenylmethane.

Apart from experiments on the action of phosphorous trichloride and of Menshutkin's acid chloride on ethanedithiol, we have carried out trials on the action of phosphorous trichloride on ethylenediamine with the aim of preparing the corresponding cyclic phosphorous derivatives. Both phosphorous trichloride and Menshutkin's acid chloride react with anhydrous ethylenediamine, and crystalline ethylenediamine hydrochloride is precipitated, but we did not succeed in isolating the reaction product.

EXPERIMENTAL

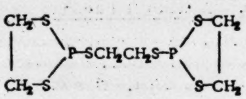
1. Action of Phosphorous Trichloride on Ethanedithiol

Freshly distilled phosphorous trichloride (65.6 g: 1 mole per mole of ethanedithiol) was added to ethanedithiol (45 g; b.p. 146° [6]) dissolved in dry ether (250 ml). When the whole of the phosphorous trichloride had been added, the reaction mixture was heated on the water-bath at 50° for 20 min. A crystalline precipitate (16.3 g) was formed. The liquid part was vacuum-distilled from an Arbuzov flask. A substance

(50.5 g; 66.5%), b.p. 102-103°/10 mm, corresponding in analysis to the required chlorido ester, was obtained. Colorless liquid, fumes strongly in air; d_0^{20} 1.5297; n_D^{20} 1.6700; found MR_D 38.91; calculated MR_D 38.79.

Found %: P 19.93; Cl 21.67; S 40.22
$C_2H_4S_2PCl$. Calculated %: P 19.55; Cl 22.35; S 40.42

After being recrystallized twice from dry benzene, the crystalline precipitate melted at 130°. It corresponded in analysis to the reaction product from 2 mol. phosphorous trichloride and 3 mol. ethanedithiol:



Found %: P 18.41; S 56.99
$C_6H_{12}S_6P_2$. Calculated %: P 18.31; S 56.90

A Rast molecular weight determination gave the following result:

Found: M 350
$C_6H_{12}S_6P_2$. Calculated: M 338.5

2. Action of Menshutkin's Acid Chloride on Ethanedithiol

Ethyl phosphorodichloridite (39.02 g) was added dropwise to an ethereal solution of a mixture of ethanedithiol (25 g) and pyridine (41.95 g) (cooling with snow). After separation of pyridine hydrochloride, the liquid products were vacuum-fractionated. A product (27.5 g, 57.3%), b.p. 98-99°/5 mm, was separated; d_0^{20} 1.2629; n_D^{20} 1.5922; found MR_D 45.09; calculated MR_D 44.90; Found %: P 18.17; 18.24; $C_4H_9S_2PO$. Calculated %: P 18.42.

The product is a colorless liquid having a characteristic unpleasant odor reminiscent of the odors of cyclic esters of phosphorous acid and of mercaptans. It reacts violently with concentrated nitric acid, giving bursts of flame. It reacts with cuprous chloride with formation of a crystalline product, m.p. 122-124°, which rapidly decomposes in air. The product of reaction with CuI melts at 134°; it also is unstable in air.

3. Action of Methanol on Ethylene Phosphorochloridodithioite

Ethylene phosphorochloridodithioite (16 g) was added dropwise to a solution of absolute methanol (3.24 g) and pyridine (8 g) in dry ether (150 ml). The reaction mixture was cooled with snow. The pyridine hydrochloride that separated was filtered off through a Schott funnel. The filtrate, after removal of solvent, was vacuum-distilled. A product (9.18 g, 59%), b.p. 97-98°/7.5 mm, was obtained: d_0^{20} 1.3426; n_D^{20} 1.6200; found MR_D 40.33; calculated MR_D 40.30; Found %: P 20.26; S 42.10; $C_3H_7S_2PO$. Calculated %: P 20.11; S 41.66.

The product is a liquid of unpleasant odor. On being cooled in snow it crystallizes to a white mass that rapidly melts at ordinary temperature. It reacts with cuprous iodide with evolution of much heat. Like the ethyl ester, it bursts into flame on being brought into contact with concentrated nitric acid.

4. Action of Ethyl Iodide on O-Ethyl Ethylene Phosphorodithioite

O-Ethyl ethylene phosphorodithioite (12 g) and ethyl iodide (11 g) were sealed in a tube and heated at 80-90° for 3 hrs. At the end of the reaction, ethyl iodide (10 g) was distilled off, and the remaining reaction products were vacuum-distilled. During distillation partial decomposition occurred, and in addition to liquid products a crystalline material came over, and this was separated mechanically. The latter was found on investigation to be dithiane (m.p. 111-112°); on being heated with methyl iodide it yielded a crystalline product corresponding in m.p. (173-174°) to the product of the addition of methyl iodide to dithiane. A liquid product (3 g; 25%), when regarded as an isomerization product), b.p. 172-174°/4 mm, was separated. A large part of the reaction products remained in the distillation flask as a dirty-pink rubberlike mass.

The fraction of b.p. 172-174°/4 mm had d_0^{20} 1.2648; n_D^{20} 1.6375.

Found %: P 18.96; S 39.95
$C_4H_9S_2PO$. Calculated %: P 18.42; S 38.13

Hydrolysis of the Product. The substance of b.p. 172-174°/4 mm (1.8 g) was heated in a sealed tube with 15% HCl (20 ml) at 165-170° for 3 hrs. The tube was opened, and the contents were found to be heterogeneous; they comprised liquid, a half-solid white mass, and some crystals; a large amount of hydrogen sulfide was evolved. After being distilled, the crystalline product melted at 111°; it was dithiane. Some more dithiane was separated by distillation from the semisolid mass. The liquid was heated on the water bath until hydrogen chloride had been completely removed. By boiling of the residue with barium carbonate, the barium salt was obtained.

Found %: Ba 39.37
$C_2H_5PS_2OBa$. Calculated %: Ba 49.40

5. Action of Methyl Iodide on Ethylene O-Methyl Phosphorodithioite

Ethylene O-methyl phosphorodithioite (6.4 g) and methyl iodide (6 g) were sealed in a tube and allowed to stand at room temperature. After standing overnight, the contents of the tube had become turbid. After the mixture had been heated at 90° for 0.5 hrs, it acquired the color of iodine. When an attempt was made to open the tube it exploded in the hands and the whole of the contents were thrown out with great force.

6. The Reaction between Ethylene O-Methyl Phosphorodithioite and Triphenylmethyl Bromide

Triphenylmethyl bromide (2.2 g) was dissolved by heat in dry benzene (5 ml). To the cooled solution ethylene O-methyl phosphorodithioite (1.05 g = 1 mol) was added. At first a homogeneous solution was formed, but after 2-3 min a precipitate began to appear; it had a pale dirty-pink color. The reaction was accompanied by scarcely appreciable evolution of heat. The product (2.5 g) was filtered off. After being recrystallized twice from dioxane and benzene it melted at 221-222°.

Found %: P 8.42; S 17.60
$C_{21}H_{19}PS_2O$. Calculated %: P 8.10; S 16.80

Rast molecular weight determination.
Found: M 373.1
$C_{21}H_{19}PS_2O$. Calculated: M 382.2

Hydrolysis of the Product of m.p. 221-222°. The product (0.8 g) and 15% HCl (15 ml) were heated in a sealed tube at 200° for 3 hrs. When the tube was opened, an odor of hydrogen sulfide was observed. Some crystals (0.2 g), much contaminated with resin, were isolated; they melted, after recrystallization from alcohol, at 92-93°. M.p. in admixture with pure triphenylmethane was also 92-93°. The liquid, which was of a brown color, was evaporated almost to dryness on the water bath. Some sort of product remained in the dish in the form of a brown incrustation.

7. Action of Triphenylmethyl Bromide on O-Ethyl Ethylene Phosphorodithioite

O-Ethyl ethylene phosphorodithioite (1.68 g) and triphenylmethyl bromide (3.23 g) were heated in benzene solution for 20 min at the boil. When the mixture was cooled, a precipitate (3.7 g) appeared. After recrystallization from benzene and gasoline, the product melted at 221-222°. It melted without depression when mixed with the previous product.

Expt. 1. Triphenylmethylphosphonic acid (0.25 g) and 15% HCl (12 ml) saturated with hydrogen sulfide were sealed in a tube and heated at 200-220° for 5 hrs. Triphenylmethylphosphonic acid was recovered unchanged (m.p. 280°).

Expt. 2. The experiment was carried out with the same amounts of the substances, but in presence of ethylene glycol (0.08 g). The same conditions of heating were observed. Triphenylmethylphosphonic acid was obtained in admixture with resinous contamination.

Expt. 3. A mixture of triphenylmethanol (0.52 g) and 15% HCl (25 ml) saturated with hydrogen sulfide was heated in a sealed tube at 200-220° for 5 hrs. The tube was cooled, and a crystalline product (0.3 g) was filtered off. M.p. after being recrystallized twice from absolute alcohol: 92-93°. In admixture with triphenylmethane it gave no depression (92-93°). In addition to triphenylmethane, some yellow needles, m.p. 119°, were obtained in very small quantity.

Expt. 4. An analogous experiment was carried out with the same amounts of triphenylmethanol and hydrochloric acid saturated with hydrogen sulfide, but ethylene glycol (1.12 g) was added. After purification of the reaction products, triphenylmethane (0.4 g, m.p. 92-93°) was obtained. The m.p. in admixture with pure triphenylmethane was again 92-93°. In addition to triphenylmethane, a small amount of crystals that melted at 117-119° to a yellow liquid were obtained.

SUMMARY

1. By the action of phosphorous trichloride on 1,2-ethanedithiol a cyclic ester of phosphorochloridodithious acid has been prepared.

2. Mixed O-alkyl ethylene esters of phosphorodithious acid have been prepared both by the action of an alcohol on ethylene phosphorochloridodithioite in presence of pyridine, and also by the action of Menshutkin's acid chloride on ethanedithiol.

3. The O-alkyl ethylene phosphorodithioites obtained react with alkyl halides (methyl iodide, triphenylmethyl bromide). The structures of the products obtained have not been established.

Received May 16, 1951

A. M. Butlerov Chemical Research Institute attached to
the V. I. Ulyanov-Lenin Kazan State University

LITERATURE CITED

[1] A. E. Arbuzov, V. M. Zoroastrova, and N. I. Rizpolozhensky. Bull. Acad. Sci. USSR. Div. Chem. Sci., 2 , 208 (1948); A. E. Arbuzov and M. M. Azanovskaya. Bull. Acad. Sci. USSR. Div. Chem. Sci., 5, 473 (1949); A. E. Arbuzov and V. M. Zoroastrova. Bull. Acad. Sci. USSR. Div. Chem. Sci. 4, 357 (1950).

[2] Walter H. C. Rueggeberg, A. Ginsburg, Walter A. Cook, J. Am. Chem. Soc. 68, 1860 (1946).

[3] R. Edward David Clark, J. Chem. Soc. 1826 (1932).

[4] M. I. Kabachnik, A. F. Divinsky, and V. V. Sidorenko. Rep. Acad. Sci.,USSR., 60, 999 (1948).

[5] A. E. Arbuzov and B. A. Arbuzov. J. Russ. Phys. Chem. Soc. 61, 225 (1929).

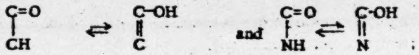
[6] N. Beverley Tucker and E. Emmet Reid, J. Am. Chem. Soc. 55, 780 (1933).

BLANK
PAGE

THE QUESTION OF THE TAUTOMERISM OF ISATIN

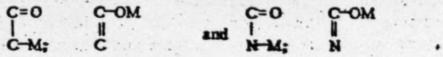
A. E. Arbuzov and M. Sh. Bastanova

For more than 80 years, right up to the present time, chemists have been concerned with the phenomena of tautomerism. The compounds that have been the subject of tautomerism studies belong to a great variety of classes of organic and inorganic compounds. The most detailed study has been made of compounds that show keto-enol and lactam-lactim tautomerism. The mobile parts of the molecules of such compounds may be represented as follows:



$$\begin{array}{c} C{=}O \\ | \\ CH \end{array} \rightleftarrows \begin{array}{c} C{-}OH \\ \| \\ C \end{array} \quad \text{and} \quad \begin{array}{c} C{=}O \\ | \\ NH \end{array} \rightleftarrows \begin{array}{c} C{-}OH \\ \| \\ N \end{array};$$

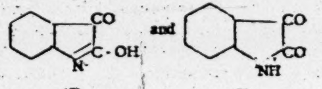
Correspondingly, the metal derivatives may be represented as:



$$\begin{array}{c} C{=}O \\ | \\ C{-}M; \end{array} \quad \begin{array}{c} C{-}OM \\ \| \\ C \end{array} \quad \text{and} \quad \begin{array}{c} C{=}O \\ | \\ N{-}M; \end{array} \quad \begin{array}{c} C{-}OM \\ \| \\ N \end{array}.$$

One of the most characteristic properties of tautomeric compounds is their ability to give, according to the conditions, derivatives that differ in structure.

Classical examples of compounds showing lactam-lactim tautomerism are isatin, carbostyril, and derivatives of these compounds.* Thus, already in 1882 Baeyer and Oekonomides [5] showed that when the sodium derivative of isatin was methylated in aqueous solution with dimethyl sulfate a methylisatin (m.p. 134°) was obtained in good yield. This compound is not hydrolyzed by alkalis, but gives "N-methylisatin-sodium". The same N-methylisatin is obtained when methyl iodide and the sodium salt of isatin in the dry state are heated together at 100° in a sealed tube. If, however, methyl iodide is allowed to react with the dry silver derivative of isatin in ether at ordinary temperature, O-methylisatin (m.p. 101-102°) is obtained. This O-derivative is hydrolyzed by aqueous alkalis, giving isatin and methanol. As yet, isatin itself has been obtained in one form only, but as it forms two series of derivatives, regarded as O- and N-derivatives, two forms may be assigned to it:



(I) (II)

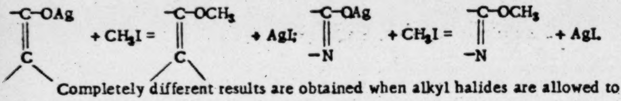
The question of the structure of tautomeric compounds is closely bound up with the question of the structure of their metal derivatives. In the literature there is a great deal of material on this question [1,5,6,7,8], and it is evident from this that the question of the structure of the salts of tautomeric compounds, in particular of the salts of isatin, is much more complicated than might have been supposed. Some investigators consider the salts to have the N-structure; others consider them to have the O-structure. It is found that the material available in the literature does not admit of definite conclusions: some investigators consider that the metal derivatives may exist in two isomeric forms, and of these, some consider the metal to be fixed in position, while others assume tautomerism; the majority of chemists, however, consider them to have the enol structure, whatever the nature of the metal may be.

If such is the position it will be found necessary to distinguish two types of replacement reaction. In the first type products of direct replacement of the metal by a radical are obtained: such reactions have been called "normal". In the second type the radical takes up a position other than that of the metal, and we have an "abnormal" reaction.

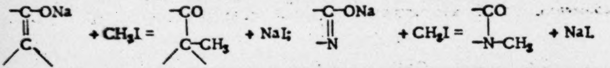
---

* See p. 446

From the enormous amount of experimental material that has been accumulated it has been possible to derive a number of guiding rules. Thus, it may be assumed that in an overwhelming majority of cases silver derivatives of tautomeric compounds on reacting with alkyl halides yield normal reaction products, i.e. the corresponding O-ethers. In this case the reactions may be represented by the following schemes:



Completely different results are obtained when alkyl halides are allowed to react with alkali derivatives. The entering radical then usually occupies a place other than that of the metal, i.e. C- or N-derivatives are obtained. In this case the reaction schemes will take the following forms:



But in many cases both reactions, normal and abnormal, proceed simultaneously, and the relative amounts of the products depend on reaction conditions (temperature, solvent, etc).

No particular difficulty is met in the explanation of normal reactions, for they are normal replacement reactions, but the explanation of abnormal reactions, particularly those of isatin and carbostyril derivatives, has turned out to be a question that is far from simple. Usually either the O- or the N-derivative (most frequently the N-derivative) is obtained, the course of the reaction depending on the conditions, the nature of the metal, etc.; in some cases both derivatives are obtained simultaneously in variable relative amounts.

The formation of N-methylisatin may evidently be represented in two different ways: we may either acknowledge that the sodium derivative has the lactam form, i.e. that the sodium is on the nitrogen, or assume formation of the O-derivative and its subsequent conversion into the N-derivative.

Thus, if we regard the salts of tautomeric compounds as O-salts, we must assume that certain changes occur during the reaction. These changes may occur either before the reaction of the metal derivative of the tautomeric compound with alkyl halide, under suitable reaction conditions, or during reaction with alkyl halide with splitting-off of the metal halide. It follows that the tautomerism of isatin (and carbostyril) derivatives, while constituting an extremely interesting field of tautomerism, cannot at present form the basis of definite conclusions on this question.

To elucidate the matter by purely chemical means will be obviously very difficult, and further work of this sort on questions of tautomerism must proceed in the direction of the accumulation and extension of the experimental material in this field: by study of a greater number of reactions, taking into account the effects due to the size and structure of the radical of the substance reacting with the tautomeric compound, to the nature of the halogen, to the temperature conditions, to the solvent, etc., and also by carrying out investigations based on physicochemical data. The study of absorption spectra has not enabled the structure of isatin to be determined, i.e. it has not shown whether the hydrogen is bound to N or to 0 [7,9,10,11].

Up to the present the only isatin derivative that has been shown to have the O-form is the O-methyl ether prepared by Baeyer. In 1939 A. E. Arbuzov [2] prepared a triphenylmethyl derivative of isatin, "O-triphenylmethylisatin", by the action of triphenylmethyl bromide and chloride on the silver and sodium salts of isatin. In all four reactions A. E. Arbuzov isolated a triphenylmethylisatin of m.p. 232-233°; since it was readily hydrolyzed by heating in a caustic soda solution on the water-bath, it was assigned the O-structure. Later, the two triphenylmethylisatins, which differ in color, were investigated spectrographically, and it was shown the yellow and the red form have identical absorption spectra. It was concluded that the red and the yellow forms of the triphenylmethyl derivative of isatin are different crystalline modifications [3]. The formation of a red and of a yellow form of triphenylmethylisatin was pointed out also in a thesis by Alimov [4].

In the present communication the results are given of a study of double decomposition reactions between salts (Na and Ag) of isatin and certain halogen compounds, including halogen-substituted ethers.

There are indications in the literature that the preparation of isatin ethers is associated with certain difficulties and is not always successful; one of the conditions for their preparation is the absolute purity of the materials used, beginning with isatin itself. The isatin used in this work was carefully purified. After recrystallization from glacial acetic acid it had a stable melting point of 198°. The starting compounds were the sodium and silver salts of isatin prepared according to the directions given in the literature.

A study was made of the reaction of salts of isatin with the following halogen compounds: benzyl bromide, benzyl chloride, (α-bromo-p-xylene, allyl iodide,) and (α-bromo-α,α-diphenyl-p-tolyl)-triphenylmethane. (α-Bromo-α,α-diphenyl-p-tolyl)-triphenylmethane was prepared, following Chichibabin, by bromination in the light of (α,α-diphenyl-p-tolyl)-triphenylmethane in carbon disulfide solution [12]. The remaining halogen compounds were prepared by the usual methods. Also, the following halogen-substituted ethers were used: bromomethyl methyl, chloromethyl methyl, bromomethyl ethyl, chloromethyl ethyl, bromomethyl propyl, and chlormethyl propyl; these were prepared from the corresponding alcohols by saturation with halogen halide in presence of formaldehyde or trioxymethylene [13]. All the starting materials were taken for reaction in the freshly prepared condition. The reactions were carried out in dry ether or in benzene, either at room temperature or at the boiling point of the solvent.

By the action of benzyl bromide or chloride on the silver or sodium salt of isatin, a benzyl isatin of m.p. 131° was obtained in all cases; it had the form of glistening sharp red needles. Benzylisatin was found to be a stable compound, not hydrolyzed by heating with dilute acids and caustic alkalis. Experiments on its isomerization in presence of benzyl bromide and on the action of methyl iodide did not give positive results.

By the action of α-bromo-p-xylene on the silver or sodium salt of isatin, (p-tolylmethyl)isatin, m.p. 141-142°, was isolated in all cases in the form of glistening long red crystals. Attempts to hydrolyze (p-tolymethyl) isatin in a solution of caustic potash or of hydrochloric acid were not successful, the (p-tolylmethyl)-isatin remaining unchanged.

By the action of bromo- or chloro-methyl methyl ether on the silver or sodium salt of isatin, the methoxymethyl ether of isatin, m.p. 90-91°, was formed in all cases. By the actionof bromo- or chloro-methyl ethyl ether on the silver or sodium salt of isatin, the ethoxymethyl ether of isatin, m.p. 85-86°, was formed in all cases. Bromo- or chloro-methyl propyl ether similarly yielded the propoxymethyl ether, m.p. 79-80°, in all cases.

The rate of reaction varied as follows: the mixed methyl ethers reacted mosted readily, then the propyl ethers, and finally the ethyl ethers. All the alkoxymethyl ethers of isatin are orange substances, readily soluble in ether and in benzene.

Hydrolysis of the methoxy-, ethoxy-, and propoxy-methyl ethers of isatin by the action of hot solutions of alkalis or acids led to formation of isatin (in almost theoretical yield), formaldehyde, and the corresponding alcohols. The readiness with which the alkoxymethyl ethers of isatin undergo hydrolysis appears to indicate that they may be regarded as orthoisomers.

When methyl iodide or benzyl bromide was heated with isatin methoxymethyl ether, high-melting products were obtained.

In addition to a study of the above reactions, a study of reactions with the halides of high-molecular-weight and unsaturated radicals was of interest. For this purpose (α-bromo-α,α-diphenyl-p-tolyl)-triphenylmethane and allyl iodide were taken. As a result of the reactions carried out, canary-yellow diphenyl (α,α,α-triphenyl-p-tolyl)-methylisatin, m.p. 250-252°, was isolated. An attempt to hydrolyze this compound with dilute alkali did not give positive results.

By the action of allyl iodide on the silver salt of isatin a resinlike product was obtained from which it was difficult to isolate anything. By the action of allyl iodide on the sodium salt a scarlet substance was isolated; this had the odor that is characteristic of substances containing the allyl radical, and it melted at 86-87°.

EXPERIMENTAL

PREPARATION OF N-BENZYLISATIN

Action of Benzyl Bromide on the Silver Salt of Isatin

Expt. 1. The silver salt of isatin (1.5 g) was added to a solution of benzyl bromide (1.09 g) in dry benzene (10 ml). The flask was stoppered and allowed to stand in a dark place at room temperature, the contents being agitated by shaking from time to time. After 1-2 hrs a noticeable change in the color of the salt had occurred. On the tenth day the precipitate was filtered off, washed and subjected to extraction with dry benzene. The weight was 1.04 g (calculated $AgBr$: 1.1 g).

From the main benzene solution, after removal of part of the solvent in a vacuum desiccator, there appeared a precipitate of benzylisatin, m.p. 118-124°. M.p. after recrystallization from ether: 130-131°.

Analysis of substance having m.p. 130-131°
Found %: N 5.25
$C_{15}H_{11}O_2N$. Calculated %: N 5.90

Action of Benzyl Chloride on the Silver Salt of Isatin

Expt. 2. The silver salt of isatin (1.3 g) was added to a solution of benzyl chloride (0.81 g) in dry benzene (10 ml). The experimental conditions were similar to those of the previous experiment. The reaction went very slowly. After two months almost the whole of the bordeaux-red silver derivative had been converted into white silver chloride. From the benzene solution, after removal of silver chloride and part of the solvent, there precipitated a yellowish-red substance, m.p. 119-125°, which after two recrystallizations from benzene melted at 130-131°.

Action of Benzyl Bromide on the Sodium Salt of Isatin

Expt. 3. The sodium salt of isatin (1.69 g) was added to a solution of benzyl bromide (1.71 g) in dry ether (20 ml). The reaction was carried out in a sealed tube at 160° for 2 hrs. When the tube was opened, there was an odor of benzyl bromide. Sodium bromide was removed, and part of the solvent was driven off under reduced pressure, when yellowish-red precipitate came down, m.p. 131-131.5° after two recrystallizations from ether. The residue after evaporation of the whole of the ether was recrystallized from aqueous alcohol and had m.p. 131-131.5° (1.05 g, 44.3%).

Action of Benzyl Chloride on the Sodium Salt of Isatin

Expt. 4. The sodium salt of isatin (1.69 g) was added to a solution of benzyl chloride (1.28 g) in dry ether (20 ml). The reaction was carried out in a sealed tube. The tube was heated for 2 hrs at 140° and 2 hrs at 160°. The result was similar to that of the previous experiment, but a greater amount of unchanged salt was left. From the ethereal solution after removal of part of the solvent a precipitate was formed of a substance of m.p. 126-127.5°, and this melted after two recrystallizations from alcohol at 131-131.5° (0.85 g altogether, 35.8%).

Melting-point determinations on mixtures of the substances obtained in the preceding experiments gave full coincidence: m.p. of mixture of substances from Expt. 1 and 4, 131-131.5°; from Expt. 2 and 4, 131-131.5°; from Expt. 3 and 4, 131-131.5°.

PREPARATION OF (p-TOLYLMETHYL)-ISATIN

Action of α-Bromo-p-xylene on the Silver Salt of Isatin

The silver salt of isatin (1.27 g) was added to a solution of α-bromo-p-xylene (0.93 g) in dry benzene (15 ml). The flask was stoppered and allowed to stand in a dark place. From time to time the contents were agitated. The reaction began very soon, but proceeded slowly. After 48 hrs the products were treated as in Expt.1. From the benzene solution a substance m.p. 138-139° was isolated. M.p. after recrystallization from alcohol: 141° (0.8 g, 70%).

Analysis of substance, m.p. 141°
Found %: N 5.08
$C_{16}H_{13}O_2N$. Calculated %: N 5.57

Action of α-Bromo-p-xylene on the Sodium Salt of Isatin

The sodium salt of isatin (1.68 g) was added to a solution of α-bromo-p-xylene (1.84 g) in dry ether (10 ml). The reaction was carried out in a sealed tube for 2 hrs at 100°. From time to time heating was interrupted and the contents of the tube were mixed. The contents of the tube were filtered, and the precipitate was washed with ether. A dirty greasy red substance smelling of α-bromo-p-xylene separated from the ethereal solution after evaporation of ether; it was recrystallized three times from alcohol and had m.p. 140.5-141° after the first recrystallization, and 141° after the second and third recrystallizations (1.15 g, 45%). M.p. of mixture of substances obtained in this and preceding experiments: 140-141.5°.

Benzylisatin and (p-tolylmethyl)-isatin crystallized out in all of the experiments as glistening well-formed sharp yellowish-red needles. Concentrated ether and benzene solutions of these are red, but they become yellow on dilution.

PREPARATION OF THE METHOXYMETHYL ETHER OF ISATIN

Alkoxymethyl ethers of isatin were prepared as follows. A round-bottomed flask was connected through a two-way adapter to a reflux condenser carrying a thermometer, which was lowered into the center of the reaction mixture, and to a dropping funnel, from which a solution of the halogen-substituted ether was added dropwise. At the end of the reaction the precipitate of halide salt was filtered off and extracted in a Soxhlet with the same solvent. The alkoxymethyl ethers of isatin, which after recrystallization had stable melting points, were isolated from the main solution and from the solution obtained after extraction. Melting-point determinations on mixtures of the alkoxymethyl ethers obtained by the use of bromine- and chlorine-substituted ethers and of silver and sodium isatin salts gave identical results. The alkoxymethyl ethers obtained from the solution from the extraction, especially when the solvents used had not been freshly dehydrated and distilled, contained small amounts of isatin, evidently owing to partial hydrolysis of the main substance present. In every experiment the yields of alkoxymethyl ether and of metal halide were determined.

All the alkoxymethyl ethers of isatin formed yellowish-orange crystals of good solubility in ether and in benzene. In solution and as finely divided powder they are yellow.

Action of Bromomethyl Methyl Ether on the Silver Salt of Isatin

A solution of bromomethyl methyl ether (1.13 g) in ether (15 ml) was added gradually to the silver salt of isatin (2.54 g) in freshly distilled ether (10 ml). The reaction started immediately, heat being evolved (30-35°). 30 min. after the whole of the bordeaux-red silver salt of isatin had been converted into yellow silver bromide, the precipitate of halide salt was separated and treated as indicated above.

From the ether solution an orange substance was isolated; after recrystallization from dry ether: 1.12 g, 63.9%; m.p. 90-91°. From the ether solution from a 4 hr extraction of the silver bromide, 0.32 g of red substance, m.p. 186-191°, was obtained, i.e. 0.4 g calculated as methoxymethyl isatin; consequently, the total yield of the methoxymethyl ether of isatin may be considered to be 1.5 g (87.2%).

Analysis of substance, m.p. 90-91°
Found %: N 6.72
$C_{10}H_9O_3N$. Calculated %: N 7.32

Action of Chloromethyl Methyl Ether on the Silver Salt of Isatin

Chloromethyl methyl ether (0.71 g) in dry ether (20 ml) was added to the silver salt of isatin (2.54 g). Reaction commenced immediately after addition of chloromethyl methyl ether, and proceeded with evolution of heat. After 30 min the precipitate of silver chloride was filtered off and extracted. An orange substance, m.p. 90-95°, (0.54 g, 28.1%) was isolated from the ether solution; its melting point remained unchanged after recrystallization from dry ether.

From the ether solution from the extraction (with 150 ml) of the silver chloride, a reddish-orange substance, m.p. 88-90° was precipitated; in the melting-point test a small amount of substance remained unmelted, but disappeared somewhat above 100°. A second extraction yielded 0.12 g of a substance of m.p. 84-106°, and a third yielded 0.15 g of a substance of m.p. 196-198° and of a red color, i.e. isatin. The total yield of methoxymethyl ether, taking this isatin into account, was 1.28 g (67.0%).

Action of Bromomethyl Methyl Ether on the Sodium Salt of Isatin

Bromomethyl methyl ether (1.2 g) in dry ether (30 ml) was added to the sodium salt of isatin (1.69 g). Appreciable reaction was noticeable after about 10 min, when slight warming occurred (23-25°). When the whole of the black sodium salt of isatin had been converted into a light-colored precipitate of sodium bromide, the latter was filtered off, washed, and extracted with ether. From the main ether solution and from the solution from the extraction of NaBr, orange crystals, m.p. 90-90.5°, (1.6 g, 87.9%) were isolated.

Action of Chloromethyl Methyl Ether on the Sodium Salt of Isatin

Chloromethyl methyl ether (0.81 g) in dry ether (20 ml) was added to the sodium salt of isatin (1.69 g). The reaction mixture was warmed on the water-bath. When the sodium salt of isatin had been converted into a white precipitate of sodium chloride, the latter was separated from the solution. From the main ether solution and from the solution from the extraction of NaCl, orange crystals, m.p. 90-91°, (1.55 g, 81.1%) were precipitated.

A melting point determination on a mixture of the substances obtained in all four reactions indicated complete identity: the mixture melted at 90.5-91.5°.

PREPARATION OF THE ETHOXYMETHYL ETHER OF ISATIN

Action of Bromomethyl Ethyl Ether on the Silver Salt of Isatin

Bromomethyl ethyl ether (1.4 g) in dry ether (25 ml) was added to the silver salt of isatin (2.54 g). Reaction with evolution of heat (the reaction mixture boiled) rapidly set in. The flask was heated for 30 min on the water-bath, and the precipitate of silver bromide was then separated and extracted with ether. The ethereal solutions yielded an orange substance, m.p. 85-86° (1.4 g, 68.3%).

It is of interest to note that during the crystallization a reddish ring of crystals formed in the higher regions; these melted at a considerably higher temperature than the main product. This, evidently, was isatin, formed by the partial hydrolysis of its ethoxyethyl ether.

Action of Chloromethyl Ethyl Ether on the Silver Salt of Isatin

Chloromethyl ethyl ether (0.68 g) in dry ether (20 ml) was added to the silver salt of isatin (1.9 g). The flask was heated in a bath of glycerol at 40-43° for one hour. The silver chloride was then separated. The ethereal solutions yielded a bright-orange substance having a golden reflex, m.p. 84-86°. (1.26 g, 82.2%). Its color was richer than that of the methoxymethyl ether. On recrystallization from ether a small amount (0.05 g) of a red undissolved substance remained; it melted at 196-198° and appeared to be isatin.

Analysis of substance, m.p. 85-86°
Found %: N 6.67
$C_{11}H_{11}O_3N$. Calculated %: N 6.83

Action of Bromomethyl Ethyl Ether on the Sodium Salt of Isatin

Bromomethyl ethyl ether (0.9 g) in dry ether (20 ml) was added to the sodium salt of isatin (1.1 g). Reaction proceeded at room temperature, but was slow. After an hour the flask was warmed on the water bath for 10 min to complete reaction. The sodium bromide was separated and washed several times with dry ether. The ethereal solutions yielded bright-orange crystals, m.p. 85-86° (0.51 g, 38.2%). A further 0.65 g of material was extracted from the mother liquor, and this, after being recrystallized twice from ether, melted at the same temperature. When the substance is left open to the air it becomes red, evidently owing to hydrolysis of the ethoxymethyl ether to isatin.

Action of Chloromethyl Ethyl Ether on the Sodium Salt of Isatin

Chloromethyl ethyl ether (0.62 g) in dry ether (20 ml) was added to the sodium salt of isatin (1.0 g), and the mixture was heated on the water-bath for 2 hrs. From the ethereal solution bright-orange crystals were separated (m.p. 85-85.5°; 0.36 g, 30%). A further 0.45 g of material was extracted from the mother liquor, and this, after being recrystallized twice from ether, had the same melting point. Mixed melting points on the ethoxymethyl ethers obtained by the four reactions described above all had the same value of 85-85.5°.

PREPARATION OF THE PROPOXYMETHYL ETHER OF ISATIN

Action of Bromomethyl Propyl Ether on the Silver Salt of Isatin

Bromomethyl propyl ether (0.93 g) in dry ether (50 ml) was added gradually to the silver salt of isatin (1.55 g). Reaction set in rapidly and proceeded with evolution of heat. At the end of the reaction the flask was heated for 10 min on the water bath. The main solution was partially distilled from a Wurtz flask. Red crystals (0.05 g, m.p. 192-198°) came out of the remaining solution on cooling. A reddish residue remained in the distillation flask (0.2 g, m.p. 164-172°); this, after recrystallization from glacial acetic acid, melted at 198-200°. It was undepressed in melting point when mixed with isatin.

The main solution after removal of isatin was partially distilled off under vacuum, when light-orange crystals having a golden reflex and of m.p. 77-78° came down. After recrystallization from ether the melting point was considerably higher, rising to 99-100°.

Analysis of Substance of m.p. 77-78°

Found %: N 6.22

$C_{12}H_{13}O_3N$. Calculated %: N 6.39

Action of Chloromethyl Propyl Ether on the Silver Salt of Isatin

A solution of chloromethyl propyl ether (0.66 g) in dry ether (20 ml) was added gradually to the silver salt of isatin (1.56 g). Reaction set in at once with evolution of heat (temprature of reaction mixture, 33°). After 30 min the flask was heated on a water bath for 10 min. From the ether solution an orange substance of m.p. 78-80° was isolated.

Analysis of substance of m.p. 78-80°

Found %: N 6.12

$C_{12}H_{13}O_3N$. Calculated %: N 6.39

Action of Bromomethyl Propyl Ether on the Sodium Salt of Isatin

A solution of bromomethyl propyl ether (2.3 g) in dry ether (30 ml) was added to the sodium salt of isatin (2.6 g). The reaction soon began, but proceeded slowly, so the mixture was heated to the boil on the bath ($\frac{1}{2}$ hr). From the ether solution an orange substance (2.1 g, 62.5%; m.p. 78-80°) was isolated.

Action of Chloromethyl Propyl Ether on the Sodium Salt of Isatin

A solution of chloromethyl propyl ether (1.1 g) in dry ether (20 ml) was added to the sodium salt of isatin (1.69 g). The reaction went more slowly than the previous one, and the reaction mixture was therefore heated for an hour. An orange substance crystallized out from the ether solution. It was recrystallized twice from dry ether (1.66 g, 75.8%; m.p. 79-80°).

Analysis of substance of m.p. 79-80°

Found %: N 6.30

$C_{12}H_{13}O_3N$. Calculated %: N 6.39

M.p. determinations on mixtures of the propoxymethyl ethers obtained in the four reactions gave 78-80°.

Hydrolysis of Benzylisatin

Benzylisatin (0.2 g) was heated in a sealed tube with 10% HCl or 10% KOH at 140-150° for one hour. After neutralization and ether extraction, benzylisatin, m.p. 131-131.5°, was recovered unchanged.

Hydrolysis of (p-Tolylmethyl)Isatin

Expt. 1. (p-Tolylmethyl)isatin (0.1 g) and 10% HCl (5 ml) were heated together in a sealed tube at 130-140° for 1 hr and at 140-150° for 1 hr. The substance that precipitated when the mixture was cool was filtered off, washed, and dried (0.8 g, m.p. 138.5-140°).

Expt. 2. (p-Tolylmethyl)isatin (0.13 g) and 10% KOH (5 ml) were heated together in a sealed tube under the same temperature conditions as in Expt. 1. All the substance was in solution. When the solution was neutralized with hydrochloric acid, an orange substance was precipitated; it was washed and dried (0.1 g, m.p. 139-140°.

The substances obtained in Expt. 1 and 2 were recrystallized together from alcohol and had m.p. 140.5-142°. In admixture with (p-tolylmethyl)isatin obtained from the sodium salt this melted at 141-142°.

Hydrolysis of Diphenyl (α, α, α-Triphenyl-p-Tolyl)-Methylisatin

The substance (0.2 g) was heated with 10% KOH (20 ml) for 1 hr. From the solution, after neutralization and ether extraction, a substance of m.p. 246-247° was isolated.

Hydrolysis of Isatin Methoxymethyl Ether in Presence of Acid

The methoxymethyl ether of isatin (0.2 g) was heated in a sealed tube with a dilute (3%) solution of hydrochloric acid at 145-150° for 2 hrs. The tube was opened, and the acid was back-titrated. From the solution isatin, m.p. 193-196°, was isolated; it was recrystallized from glacial acetic acid (0.08 g, 55%; m.p. 199-200°).

Hydrolysis of Isatin Methoxymethyl Ether in Presence of Caustic Alkali

Isatin methoxymethyl ether of m.p. 90-90.5° (0.15 g) was heated in a flask with a dilute solution of KOH (20 ml, 0.13 g KOH) for half an hour. The solution was then neutralized with hydrochloric acid and partially distilled off. Tests on the distillate for aldehyde (Schiff's reagent and ammoniacal silver nitrate) gave positive results. The remaining solution was extracted repeatedly with ether, and the extract, on evaporating down, yielded a precipitate of isatin, m.p. 194-196° rising to 199-200° after recrystallization from glacial acetic acid (0.08 g, 76.6%). The m.p. was undepressed when an admixture of pure isatin was made.

Hydrolysis of Isatin Ethoxymethyl Ether

Isatin ethoxymethyl ether of m.p. 85° (0.7 g) was heated in a flask fitted with reflux condenser with dilute KOH solution (30 ml, 0.5 g KOH) for 1 hour. The solution was then neutralized with hydrochloric acid. A part of the solution was distilled off, and qualitative tests were made for formaldehyde and ethanol. The solution gave a magenta color with Schiff's reagent and a silver mirror with ammoniacal silver nitrate; with iodine dissolved in a solution of potassium iodide and caustic potash it gave a yellow precipitate of iodoform.

The remaining solution was repeatedly extracted with ether, and from the ethereal solution, after evaporation of some of the ether, a precipitate of isatin was formed in almost quantitative yield. The melting point, after recrystallization from glacial acetic acid, was 200°; in admixture with pure isatin it melted at 199-200°.

Hydrolysis of Isatin Propoxymethyl Ether

Isatin propoxymethyl ether of m.p. 79-80° was heated in a flask under reflux with dilute sulfuric acid (40 ml) for 1 hour. The acid was then back-titrated and, as in the above-described reactions, aldehyde was detected in the solution by a qualitative reaction. The remaining solution was extracted with ether, and isatin was isolated as before, m.p. after recrystallization from glacial acetic acid 199-200° (0.32 g, 80%).

Action of Alkyl Halides on Isatin Ethers

Action of Methyl Iodide and of Benzyl Bromide on Benzylisatin

Expt. 1. Benzylisatin of m.p. 131° (0.14 g) and methyl iodide (0.4 g) were heated together in a sealed tube at 120-140° for 3 hours. After heating and cooling, the liquid had the same level. Methyl iodide was driven off under reduced pressure. The substance remaining in the tube melted at 130-131°, and in admixture with the starting material it melted at 130.5°.

Expt. 2. Some of the same benzylisatin (0.1 g) was heated with benzyl bromide for 2 hours at 100-155° and for 2 hours at 160-170°. The contents of the tube were cooled and filtered under suction, and the residue was washed repeatedly with ether. 0.08 g of material of m.p. 130-130.5° was recovered. The mixed m.p. was 130-131°.

Action of Benzyl Bromide on Isatin Methoxymethyl Ether

Isatin methoxymethyl ether (0.3 g) was heated in a sealed tube with benzyl bromide (1.5 g). Heating was for 2 hours at 150-160° and 2 hours at 175-185°. When the tube had cooled, fine crystals came down and the volume was found to be somewhat reduced (1.5-2 mm). The solution had become more reddish in color. Opening of the tube revealed no excess pressure. The precipitated crystals were filtered off and washed several times with ether (0.09 g of crystals). In the melting-point test, the substance began to change its color somewhat — from reddish yellow to grayish brown — but did melt when heated to 292°. From the benzyl bromide solution a further 0.04 g of material came down; it was washed with ether and tested for melting point, but did not melt up to 292° and gradually became darker in color as the temperature rose above 300°.

Action of Benzyl Bromide on Isatin Ethoxymethyl Ether

Isatin ethoxymethyl ether (0.11 g) and benzyl bromide (0.38 g) were heated together in a sealed tube for 2 hours at 160-170°. The solution became more yellowish in color. The benzyl bromide was distilled off under reduced pressure, and a yellow substance (0.6 g) was isolated. It was washed several times with ether and then tested for melting point. At above 240° it began to go reddish, above 260° it began to go brown, and finally it became almost black and melted (270-273°).

SUMMARY

1. By the action of the bromomethyl and chloromethyl ethers of methyl, ethyl, and propyl alcohols on the sodium and silver derivatives of isatin, the corresponding isatin ethers have been prepared: isatin methoxymethyl ether of m.p. 90-91°, isatin ethoxymethyl ether of m.p. 85-86°, and isatin propoxymethyl ether of m.p. 79-80°.

2. All the derivatives obtained were readily hydrolyzed.

3. The hydrolysis products of the methoxy-, ethoxy-, and propoxy-methyl ethers of isatin were isatin (obtained in almost quantitative yield), formaldehyde, and the corresponding alcohols.

4. By the action on the sodium and silver derivatives of isatin of (α-bromo-α,α-diphenyl-p-tolyl)-triphenylmethane, of benzyl bromide and chloride, and of α-bromo-p-xylene there were obtained diphenyl-(α,α,α-triphenyl-p-tolyl)-methylisatin of m.p. 250-252°, benzylisatin of m.p. 131°, and (p-tolylmethyl)-isatin of m.p. 141-142°.

5. Attempts to hydrolyze the substances of m.p. 131°, 141-142°, and 250-252° did not give satisfactory results: the substances were recovered unchanged. The question of their structures remains an open one.

6. When the methoxymethyl and ethoxymethyl derivatives of isatin are heated with methyl iodide or with benzyl bromide, high-melting products are obtained.

7. Benzylisatin remains unchanged in presence of methyl iodide or of benzyl bromide.

Received February 20, 1952

S. M. Kirov Kazan Chemical-Technological Institute

LITERATURE CITED

[1] A. E. Arbuzov. Bull. Acad. Sci., 211 (1939).

[2] A. E. Arbuzov. Bull. Acad. Sci. USSR. Div. Chem. Sci., No.1, 89 (1940).

[3] A. E. Arbuzov and O. M. Shapshinskaya. Trans. Kazan Chem.-Tech. Inst., 1951.

[4] P. I. Alimov. Dissertation 141, 1944.

[5] A. Baeyer and S. Oekonomides, B. 15, 2093 (1882); 16, 2193 (1883).

[6] W. Hartley and L. Dobbie, J. Chem. Soc. 75, 640 (1889).

[7] A. Hantzsch and coworkers. B. 54, 1221 (1921); 54, 1257 (1921); 55, 3180, 3186 (1922); Ber. 56, 2110 (1923); 58, 685 (1925).

[8] G. Heller. Ber. 40, 1291; 49, 2457; 50, 1199; 51, 180, 1270; Ber. 52, 437; 53, 1545; 54, 2212 (1921); 55, 1006, 2681 (1922); 56, 1591 (1933).

[9] R. Morton and E. Rogers. J. Chem. Soc. 127, 2698 (1925).

[10] L. Dabrowsky and L. Marchlewsky, Bull. Soc. chim. 53, 946 (1933).

[11] R. G. Ault, E. Hirst and R. Morton. J. Chem. Soc. II, 1653 (1935).

[12] A. E. Chichibabin, Ber. 37, 4713 (1904).

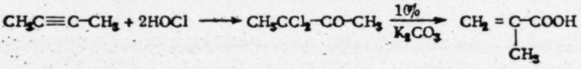
[13] A. Karvonen, C. 11, 1269 (1912).

BLANK
PAGE

SYNTHESIS AND PROPERTIES OF α-ALKOXYETHYL ESTERS OF UNSATURATED CARBOXYLIC ACIDS ("ACYLALS")

M. F. Shostakovsky, N. A. Gershtein, Ya. L. Raskin, and L. E. Ostroumova

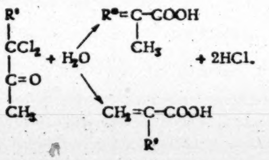
Acrylic acids and their derivatives, which have a conjugated system of double bonds $>C{=}C{-}C{=}O$, readily enter into various reactions, particularly polymerization and copolymerization reactions. Polymers of acrylates, and particularly of methacrylates and also of acrylic acids, are valuable materials (films, plastics, Plexiglas, Crystalite, etc.), which have been widely applied in industry. The method of synthesis of this class of compound was sketched out by Favorsky [1] already in 1894 in terms of the reaction that he discovered between distributed acetylene hydrocarbons and hypochlorous acid:



$$CH_3C{\equiv}C{-}CH_3 + 2HOCl \longrightarrow CH_3CCl_2{-}CO{-}CH_3 \xrightarrow[K_2CO_3]{10\%} CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}COOH$$

This reaction was studied on the basis of many examples, and Favorsky [2] writes as follows about it: "Thus, the reaction in which unsaturated acids are formed by the action of a 10 % solution of potassium carbonate on α,α-dichloro ketones may be considered, on the basis of facts already given, to be a general reaction, and in view of this it may be expressed by the following series of equations:

$$R'{-}CO{-}CHCl_2 + H_2O \longrightarrow R'' = CH{-}COOH + 2HCl. \qquad (I)$$



(II)

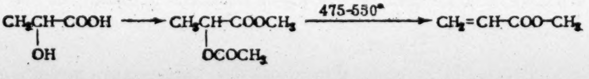
However, the development of industry based on acrylic acids was delayed by the absence of simple and accessible methods for the synthesis of acrylic esters. Thus, up to 1927 methyl acrylate was obtained by a very complex route:

$$CH_2{=}CH{-}CH_2OH + Br_2 \longrightarrow CH_2Br{-}CH_2OH \xrightarrow{O} CH_2Br{-}CHBr{-}COOH \xrightarrow{ROH} CH_2Br{-}CHBrCOOR \xrightarrow{Zn}$$
$$\longrightarrow CH_2{=}CH{-}COOR\ (R{=}CH_3).$$

Later, an economically sounder method for the preparation of methylacrylate via 2-chloroethanol was developed:

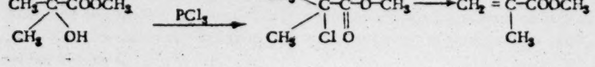
$$HOCH_2{-}CH_2Cl \xrightarrow{NaCN} HOCH_2{-}CH_2CN \xrightarrow[H_2SO_4]{CH_3OH} CH_2{=}CH{-}COOCH_3.$$

As well as by this method, methyl acrylate is now prepared in industry by a pyrolysis method from lactic acid:

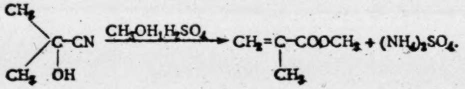


$$CH_3\underset{\displaystyle OH}{\underset{|}{CH}}{-}COOH \longrightarrow CH_3\underset{\displaystyle OCOCH_3}{\underset{|}{CH}}{-}COOCH_3 \xrightarrow{475\text{-}550^\circ} CH_2{=}CH{-}COO{-}CH_3$$

Still wider application has been accorded the methacrylates, which polymerize more readily and give products having more desirable properties; practical interest in them is therefore high. However, the synthesis of esters of methacrylic acid, particularly the methyl ester, also requires complex methods [3,4]:

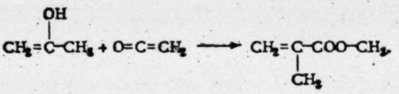


which does not differ in principle from Favorsky's method:



$$(CH_3)_2C(OH)-CN \xrightarrow{CH_3OH,\ H_2SO_4} CH_2=C(CH_3)-COOCH_3 + (NH_4)_2SO_4.$$

Quite recently a method has been described for the preparation of methacrylic esters by the condensation of ketones with ketenes in presence of sulfanilic acid derivatives as catalysts [5]:

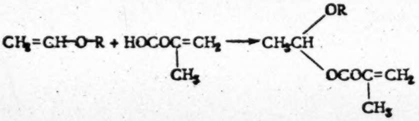


$$CH_2=C(OH)-CH_3 + O=C=CH_2 \longrightarrow CH_2=C(CH_3)-COO-CH_3.$$

The higher esters of acrylic acids are synthesized by alcoholysis of the methyl esters. It is natural, therefore, that the interest of chemists in the preparation of more and more new acrylic acid derivatives continues unabated.

The vinyl ethers, which also are very reactive compounds, have recently become industrial products, thanks mainly to the work of Favorsky and Shostakovsky. That is why the combination of vinyl ethers and acrylic acids opens up the prospect of preparing new, practical, valuable products and is enriching chemistry with new, extremely interesting compounds.

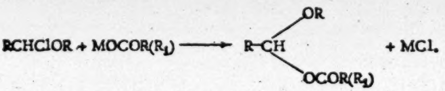
The aim of the present investigation was to prepare from vinyl ethers and methacrylic acid a series of new ester-like substances of an unsaturated nature, viz. the acylals, and to study their properties.



$$CH_2=CH-O-R + HOCOC(CH_3)=CH_2 \longrightarrow CH_3CH(OR)(OCOC(CH_3)=CH_2)$$

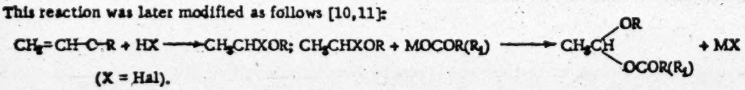
In the previous communication [6] a method was described for the synthesis of 1-alkoxyethyl esters by the addition of carboxylic acids to vinyl ethers. This reaction has greatly simplified the preparation of acylals. The previously known methods for the preparation of acylals via unstable α-halo ethers and salts of carboxylic acids are more complex [7-9]:

$$RCHO + ROH + HCl \longrightarrow RCHClOR$$



$$RCHClOR + MOCOR(R_1) \longrightarrow R-CH(OR)(OCOR(R_1)) + MCl.$$

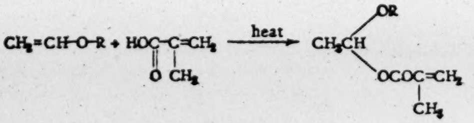
This reaction was later modified as follows [10,11]:



$$CH_2=CH-O-R + HX \longrightarrow CH_3CHXOR;\ CH_3CHXOR + MOCOR(R_1) \longrightarrow CH_3CH(OR)(OCOR(R_1)) + MX$$

(X = Hal).

For the synthesis of unsaturated acylals we have made use of the method of direct addition of methacrylic acid to vinyl ethers:



$$CH_2=CH-O-R + HOC(=O)-C(CH_3)=CH_2 \xrightarrow{heat} CH_3CH(OR)(OCOC(CH_3)=CH_2)$$

It was found that this reaction proceeds fairly smoothly and gives unsaturated acylals in 65-80% yield. A study was made also of the effect of the addition of catalysts (mineral acids) on the yield, but the expected increase in yield was not obtained.

In the present communication we describe the synthesis and properties of α-cyclohexyloxy-, α-benzyloxy-, and α-phenoxy-ethyl methacrylates. The starting substances were methacrylic acid and the vinyl ethers of cyclohexanol, benzyl alcohol, and phenol. In a number of patents [12] on the vinylation of hydroxy compounds, the above vinyl ethers are included among those listed, but the constants and yields of the first two are practically passed over.

We synthesized these two ethers by the method of Favorsky and Shostakovsky [13], slightly modified. The yields of vinyl ether were 68-69 %. The acylals prepared from them are liquids having a characteristic ethereal odor; they polymerize when heated in presence of peroxide catalysts. The structural peculiarities of these acylals, which contain in their molecules a number of conjugated double bonds, are manifested in their molecular refractions by an increased exaltation. Our results are given in Table 1.

Hydrolytic splitting of these acylals proceeds as follows:

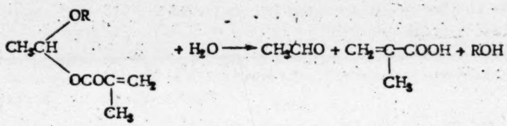
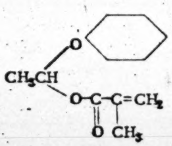
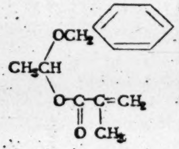
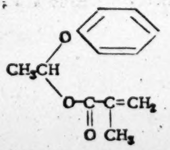


TABLE 1

Molecular Refractions of Acylals

Compound	MR		Difference
	Found	Calculated	
	59.02	58.246	0.774
	62.58	61.463	1.117
	57.75	56.845	0.905

However, the rate at which this decomposition occurs depends to an appreciable extent on the structure of the radical R. When R is an aliphatic radical, hydrolysis is brought about fairly rapidly in the cold by means of 2-5% solutions of mineral acids (simple shaking for 2-3 min). When R is C_6H_{11} (cyclohexyl), hydrolysis under the same conditions requires 25-30 min. When R is $C_6H_5CH_2$ about an hour is required, and when R is C_6H_5 heating at 100° for 3-5 hrs is required. Thus, with respect to the effect of the radical R on the rate of acid hydrolysis of the acylals studied, the following series may be written:

$$\text{Alkyl} > C_6H_{11} > C_6H_5CH_2 > C_6H_5.$$

The densities of acylals having a radical R containing an aromatic nucleus are greater than unity.

EXPERIMENTAL

Synthesis of Cyclohexyl Vinyl Ether $CH_2=CH{-}O{-}C_6H_{11}$ (I)

Cyclohexanol (100 g) and solid caustic potash (10 g) were loaded into a 500-ml rotating autoclave and heated with acetylene, which was admitted in portions under a pressure of 14-18 atm, to 148-150°. At this temperature heating was continued for 1.5-2 hrs for each portion of acetylene. At the end of the reaction a mobile brown liquid (115.5 g) was obtained. The autoclave was washed with ether. The ether extracts were added to the main product, which had been diluted with ether. The ethereal solution of the product was washed several times with water in a separating funnel. All the wash waters were shaken, in their turns, 2-3 times with ether. All the ether extracts were dried with calcined potassium carbonate and filtered. The solvent was removed, and the residue vacuum-fractionated. Cyclohexyl vinyl ether (87.5 g, 68.6%), b.p. 52-54°/23 mm was obtained. Similarly, from 210 g of cyclohexanol and 20 g of caustic potash under the same conditions 182 g of cyclohexyl vinyl ether was obtained (69.5% of cyclohexanol). Cyclohexyl vinyl ether is a colorless, transparent, very mobile liquid having an ethereal odor; b.p. 52-54° at 23 mm; b.p. 63° at 37 mm; b.p. 47.2-47.5° at 15 mm; n_D^{20} 1.4547; d_4^{20} 0.888; found MR_D 38.50; calculated for $C_8H_{14}O|^{=}$ MR_D 38.12. B.p. 147-148° [14].

Found %: C 76.30; H 11.33
$C_8H_{14}O$. Calculated %: C 76.19; H 11.11

The cyclohexyl vinyl ether was hydrolyzed by means of a 2% solution of sulfuric acid. The acetaldehyde formed was determined quantitatively by Ripper's method [15]

Found %: AcH 98.11 (of theoretical)

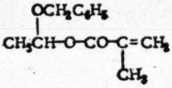
Synthesis of Benzyl Vinyl Ether $CH_2=CH-OCH_2-C_6H_5$ (II)

The conditions for the synthesis of benzyl vinyl ether were the same as for the synthesis of cyclohexyl vinyl ether. From 110 g of benzyl alcohol (freshly distilled) and 11 g of caustic potash, with introduction of acetylene under a pressure of 18 atm, 84.7 g (62%) was obtained. Similarly, from 80 g of benzyl alcohol and 8 g of caustic potash 67.5 g (68%) of benzyl vinyl ether was obtained. B.p. 81.5° at 22 mm; b.p. 82.5° at 24 mm; n_D^{20} 1.5185; d_4^{20} 0.9711; found MR_D 41.87; calculated for $C_9H_{14}O|^{=}_4$ MR_D 41.337. [16]; b.p. 183-184°; n_D^{20} 1.5160; d_4^{20} 0.9710.

Found %: C 80.40; H 7.63
$C_9H_{14}O$. Calculated %: C 80.55; H 7.51
Found %: AcH 98.24 (of theoretical)

SYNTHESIS OF ACYLALS

1. Synthesis of 1-Benzyloxyethyl Methacrylate



$$CH_3\underset{|}{\overset{OCH_2C_6H_5}{CH}}-O-CO-\underset{CH_3}{\underset{|}{C}}=CH_2$$

Expt. 1 (without catalyst). A mixture of freshly distilled methacrylic acid (10.8 g, 0.12 mole), b.p. 160-161°, n_D^{25} 1.4113 and 20 g (0.15 mole) having the above-indicated constants were heated in a sealed tube on a boiling water bath for 4.5-5 hrs. The reaction products were fractionally distilled in a stream of nitrogen, which was passed through an alkaline solution of pyrogallol, through sulfuric acid, and over solid caustic potash or soda. A substance was obtained (13.9 g, 78.5%) of b.p. 82-82.2°/14 mm.

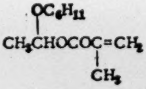
Expt. 2 (in presence of H_2SO_4 as catalyst). Freshly distilled methacrylic acid (5 g) and benzyl vinyl ether (12.7 g) were introduced into a three-necked flask fitted with reflux condenser and mechanical, mercury-sealed stirrer; with constant stirring sulfuric acid (0.05% on methacrylic acid taken) was added as a 2% alcoholic solution. There was a slow spontaneous rise in the reaction temperature from 17 to 50° in 1 hr 15 min, and the temperature was then maintained at this level for 3 hrs. The reaction mass was left overnight and then vacuum-distilled in a stream of nitrogen in presence of antioxidants. The yield of pure substance, b.p. 83.7-84°/15 mm, was 9.9 g (77.6%).

1-Benzyloxyethyl methacrylate is a colorless liquid having an ethereal, camphor-like odor; b.p. 82-82.2° at 14 mm; b.p. 83.7-84° at 15 mm; n_D^{20} 1.5008; d_4^{20} 1.0367; found MR_D 62.58; calculated $C_{13}H_{16}O_3|^{=}_4$ MR_D 61.463.

Found %: C 70.48; H 7.00
$C_{13}H_{16}O_3$. Calculated %: C 70.92; H 7.33

Found by hydrolysis with 2% sulfuric acid: AcH 98.01% of theoretical.

2. Synthesis of 1-Cyclohexyloxyethyl Methacrylate



$$CH_3\underset{|}{\overset{OC_6H_{11}}{CH}}OCO\underset{CH_3}{\underset{|}{C}}=CH_2$$

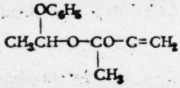
Expt. 1 (without catalyst). By proceeding under the conditions of the previous synthesis from 8.6 g (0.1 mole) of the freshly distilled acid and 20.6 g (0.16 mole) of cyclohexyl vinyl ether, heated in a sealed tube for 5 hrs, we obtained 16.5 g (77.8%) of the required acylal, b.p. 114-115°/20 mm.

Expt. 2 (in presence of H_2SO_4 as catalyst). By proceeding under the conditions of the previous synthesis from 7 g of freshly distilled methacrylic acid and 19.4 g of cyclohexyl vinyl ether in presence of 0.05% of sulfuric acid, we obtained 13.65 g (79.1%) of acylal, b.p. 112-112.5°/19 mm.

1-Cyclohexyloxyethyl methacrylate is a colorless, transparent liquid having a characteristic ethereal odor; b.p. 112-112.5° at 19 mm; b.p. 113.5-114° at 20 mm; b.p. 115-115.2° at 20 mm; n_D^{20} 1.4560; d_4^{20} 0.9776; found MR_D 59.02, calculated $C_{12}H_{20}O_3\overline{F}$ MR_D 58.246.

Found %: C 67.84; H 9.50
$C_{12}H_{20}O_3$. Calculated %: C 67.88; H 9.50
Found %: AcH 98.07

3. Synthesis of 1-Phenoxyethyl Methacrylate



$$\begin{array}{c}OC_6H_5\\|\\CH_3CH{-}O{-}CO{-}C{=}CH_2\\\qquad\qquad\quad|\\\qquad\qquad\quad CH_3\end{array}$$

The synthesis of 1-phenoxyethyl methacrylate was carried out by means of heat in presence of catalysts. The addition of methacrylic acid to phenyl vinyl ether requires more severe conditions (higher temperature and more prolonged heating), and these lead to polymerization of the phenoxyethyl methacrylate formed.

It follows from the results given in Table 2 that with an excess of vinyl ether of up to 30% and with various periods of heating the yield of acylal remains practically constant. The distillation of phenoxyethyl methacrylate was carried out in a stream of nitrogen in presence of 0.5% of toluylenediamine. 1-Phenoxyethyl methacrylate has the following constants: b.p. 98-99° at 15 mm; b.p. 129-130° at 20 mm; n_D^{20} 1.5030; d_4^{20} 1.0561; found MR_D 57.75; calculated $C_{12}H_{14}O_3\overline{F}_4$ MR_D 56.845.

Found %: C 70.40; H 7.00
$C_{12}H_{14}O_3$. Calculated %: C 69.85; H 6.84

TABLE 2

Synthesis of Phenoxyethyl Methacrylate

Expt. No.	Ratio of reagents		Catalyst (mol H_2SO_4 per mol acid)	Max. reaction temp. °C	Duration of heating	Yield of acylal after fractionation (%)
	Ether (mol)	Acid (mol)				
1	1.28	1	$43 \cdot 10^{-5}$	60	1 hr 30 min exothermic reaction and 1 hr further heating at 60°	93.2
2	1.26	1	$43 \cdot 10^{-5}$	60	1 hr 30 min exothermic reaction and 1 hr 30 min further heating at 60°	90.8
3	1.18	1	$43 \cdot 10^{-5}$	70	1 hr 15 min exothermic reaction and 2 hrs 30 min further heating at 70°	92.4

Found by hydrolysis with 5% sulfuric acid: AcH 97.44 % of theoretical.

SUMMARY

1. Unsaturated acylals have been synthesized for the first time from aralkyl vinyl, aryl vinyl, and cyclohexyl vinyl ethers and methacrylic acid.

2. The properties of the acylals obtained have been described.

3. The relation between the rate of hydrolysis of these acylals and the structure of the ether radical has been found, and on its basis radicals have been placed in a series corresponding to a diminishing tendency in the acylals to hydrolysis.

Received September 23, 1951

Institute of Organic Chemistry of the
Academy of Sciences of the USSR

LITERATURE CITED

[1] A. E. Favorsky. Investigation of Isomeric Changes in the Series of Carbonyl Compounds, Chlorinated alcohols, and halogen-substituted ethers. Doctorate thesis. St. Petersburg. 1895 (quoted from Selected Works of A. E. Favorsky, Acad. Sci. USSR Press, Moscow-Leningrad, 1940, p. 93).

[2] A. E. Favorsky. Ibid., p. 109.

[3] Barret, U. S. P. 2305663 (1943) (quoted from the compilation Monomers Blant Marx, Hohenstein, N.Y. 1949).

[4] Warne, U.S. P. 2352582 (1944).

[5] G. Frank, U. S. P. 2461016 (1949); Chem. Abs. 43, 3838 (1949).

[6] N. A. Gershtein and M. F. Shostakovsky. J. Gen. Chem. 18, 2, 1989 (1948).

[7] Friend, E. Clark, S. F. Cox and E. Mack, J. Am. Chem. Soc. 39, 712 (1917).

[8] J. W. Farren, H. R. Fife, F. E. Clark et al, J. Am. Chem. Soc. 47, 2422 (1925).

[9] M. N. Paloma and J. Salmi et al., Ber. 68, 305 (1935).

[10] I. G. Farbenind, E. P. 352070 (1930); C. 1931, II 2756.

[11] M. F. Shostakovsky and A. V. Bogdanova. J Gen. Chem. 17, 565-574 (1947); 20, Ber. 7, 1315, 1326 (1950).

[12] E. J . Gasson, F. E. Salt, F. P. 952158 (1949); C 1950, II, 1875. Schwed. P. 82550 (1934); C. 1936, II, 3846. W. Reppe, U.S. P. 1959927 (1934); Chem.Abs. 28, 4431 (1934); U. S. P. 2017355 (1935); C. 1936, II, 1796.

[13] A. E. Favorsky and M. F. Shostakovsky. Auth. Cert. No. 59308 (1941).

[14] German Patent 550495 (1929); Chem. Abs. 26, 4825 (1932).

[15] M. Ripper, Monatsh. 21, 1079 (1900).

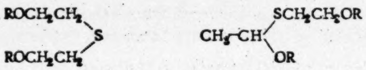
[16] M. F. Shostakovsky and M. S. Burmistrova. J. Appl. Chem. 15, No. 4, 260 (1942).

SYNTHESIS OF SULFUR COMPOUNDS BY THE AID OF VINYL ETHERS

COMMUNICATION 5. SOME NEW α,β- AND β,β'-DIALKOXY DERIVATIVES OF DIETHYL SULFIDES

E. N. Prilezhaeva, E. S. Shapiro, and M. F. Shostakovsky

In the present communication a description is given of the conditions of synthesis and also certain properties of α,β- and β,β'-dialkoxy derivatives of diethyl sulfide obtained from isobutyl vinyl and isoamyl vinyl ethers. The reactions of these ethers have confirmed all the regularities that have been established previously for the addition reaction between gaseous hydrogen sulfide and vinyl ethers in dioxane in presence of HCl as catalyst [1]. The yield of reaction products, a mixture of isomeric dialkoxy derivatives of diethyl sulfide (I, II, III, and IV), is 80-85%.

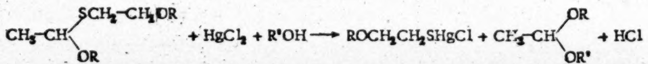


$$\left.\begin{matrix}ROCH_2CH_2\\ROCH_2CH_2\end{matrix}\right>S \qquad CH_3-CH\left<\begin{matrix}SCH_2CH_2OR\\OR\end{matrix}\right.$$

(I), (III) (II), (IV)

(I), (II) R = iso-C_4H_9 (III), (IV) R = iso-C_5H_{11}

The percentage contents of isomers in this mixture were determined by the aid of the analytical method proposed in the same communication [1]; it is based on the decomposition of sulfides II and IV in presence of an alcoholic solution of mercuric chloride (equation 1).•

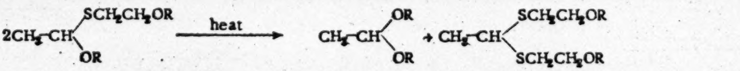


$$CH_3-CH\left<\begin{matrix}SCH_2-CH_2OR\\OR\end{matrix}\right. + HgCl_2 + R'OH \longrightarrow ROCH_2CH_2SHgCl + CH_3-CH\left<\begin{matrix}OR\\OR'\end{matrix}\right. + HCl \qquad (1)$$

(V),(VI)

(V) R = iso-C_4H_9 (VI) R = iso-C_5H_{11}

The new representatives of the series of α,β-dialkoxy derivatives of diethyl sulfide, which have a monothioacetal structure, are similar to those described previously [3] and differ greatly in thermal stability and chemical properties from the β,β'-dialkoxydiethyl sulfide series. Thus, prolonged storage, heating, and particularly treatment with acids leads to disproportionation with formation of equimolecular amounts of dialkyl acetals (VII, VIII) and of the corresponding β,β'-alkoxyethyl mercaptals (IX, X) according to equation 2:

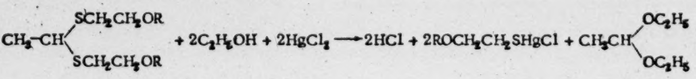


$$2CH_3-CH\left<\begin{matrix}SCH_2CH_2OR\\OR\end{matrix}\right. \xrightarrow{\text{heat}} CH_3-CH\left<\begin{matrix}OR\\OR\end{matrix}\right. + CH_3-CH\left<\begin{matrix}SCH_2CH_2OR\\SCH_2CH_2OR\end{matrix}\right. \qquad (2)$$

(VII), (VIII) (IX) (X)

(VII), (IX) R = iso-C_4H_9 (VIII), (X) = iso-C_5H_{11}

Acetaldehyde bis(β-alkoxyethyl mercaptals, like other members of the mercaptal class [4], do not give stable complex salts with mercuric chloride, but react with the latter according to Equation 3 with formation of alkoxyethylmercaptomercury chlorides (V, VI) identical with those obtained from the corresponding sulfides (II, IV) (Equation 1).



$$CH_3-CH\left<\begin{matrix}SCH_2CH_2OR\\SCH_2CH_2OR\end{matrix}\right. + 2C_2H_5OH + 2HgCl_2 \longrightarrow 2HCl + 2ROCH_2CH_2SHgCl + CH_3CH\left<\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix}\right. \qquad (3)$$

• A similar analytical method was proposed earlier by Holmberg [2] for the quantitative determination of derivatives of α,α'-(methylenedithio)-diacetic acid (bis-(carboxymethyl) mercaptals and mercaptoles).

Thus, new examples have been found that confirm the characteristic chemical behavior of sulfides having alkoxy or alkylmercapto groups on the carbon adjacent to the sulfur atom.

EXPERIMENTAL*

1. Action of Hydrogen Sulfide on Isobutyl Vinyl Ether

a) To 25 g of isobutyl vinyl ether there was added, after a preliminary 15 min passage of hydrogen sulfide through the system, 0.2 ml of 17% catalyst (0.1% by wt of HCl on ether taken). The experiment was carried out under a pressure of hydrogen sulfide at room temperature for 12.5 hr. No appreciable rise in temperature was to be observed. The reaction was then continued for an hour at 43°. After 13.5 hr the increase in weight of the reaction mass was 2 g.

Fractional distillation gave:

Unchanged ether – 4 g
Fraction 1, b.p. 33-34° at 3.5 mm – 0.5 g
Fraction 2, b.p. 100-106° at 2.5 mm – 19.8 g; n_D^{20} 1.4485
Residue, a brown viscous substance – 0.8 g.

Fraction 1 gave a qualitative reaction for mercaptan. Fraction 2 was a mixture of the isomeric sulfides I and II; yield 80.5% of the ether. Amount of α,β-isomer (II) by titration: 55.3; 55.1%.

b) 106 g of isobutyl vinyl ether, 0.1 ml of 26.4% catalyst (0.03% by wt on ether of HCl). The experiment was carried out at 50°. After 3 hrs, very vigorous absorption of hydrogen sulfide began. After 30 hrs the increase in weight was 16.5 g. Fractionation of the product yielded unchanged ether (6.6 g), and the residue was fractionated twice and yielded the following fractions: in the trap (at –75°) 2.7 g, n_D^{20} 1.4078; [illegible]

Fraction 1, 34-37° at 4 mm – 1.8 g; n_D^{20} 1.4120
Fraction 2, 70-100° at 4 mm – 1.9 g; n_D^{21} 1.4430
Fraction 3, 105-113° at 4 mm – 101.4 g; n_D^{21} 1.4505
Fraction 4, 150-160° at 4 mm – 7.5 g; n_D^{23} 1.4691

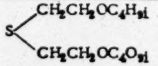
By repeated fractionation of the product collected in the trap and of Fraction 1, diisobutyl acetal (VII) was isolated, and from Fraction 4, bis(β-isobutoxyethyl) mercaptal (IX) was isolated; both substances are disproportionation products from α,β-isobutoxyethyl sulfide (II) and are characterized below in detail. The yield of the sulfide fraction (3) was 87%. Amount of α,β-isomer (II) by titration: 26.7; 26.4 %.

Thus, under conditions of lower acidity the percentage of α,β-isomer in the mixture is reduced, but rise in the reaction temperature is accompanied by increase in the extent of disproportionation of the α,β-sulfide with formation of fractions 1 and 4.

2. Properties of the Isomeric Diisobutoxy Derivatives of Diethyl Sulfide (I and II)

The mixture of disulfides was resolved into the practically pure isomers by vacuum fractionation through a column of 18-20 theoretical plates.

1) β,β'-Dibutoxydiethyl Sulfide



$$S\begin{cases}CH_2CH_2OC_4H_{9i}\\CH_2CH_2OC_4O_{9i}\end{cases}\qquad(I)$$

is a liquid having practically no distinct odor. It is an extremely stable substance; b.p. 124° at 5 mm; 116.2-116.4° at 3.5 mm; n_D^{20} 1.4510, d_4^{20} 0.9126; found MR_D 69.16; calculated MR_D 68.88.

Found %: C 61.48; 61.49; H 11.18; 11.20; S. 13.63; 13.55
$C_{12}H_{26}O_2S$. Calculated %: C 61.49; H 11.18; S 13.68;

β,β'-Diisobutoxydiethyl sulfide (I) does not give an acid reaction in presence of mercuric chloride, but forms a complex compound with mercuric chloride that crystallizes in large plates: $C_{12}H_{26}O_2S\cdot HgCl_2$, m.p. 47°.

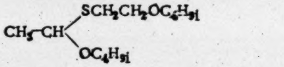
Found %: S 6.20; 6.14
$C_{12}H_{26}O_2S\cdot HgCl_2$. Calculated %: S 6.31

---

* For details of procedure see Communication 2 [1].

In the literature [5] on β,β'-diisobutoxydiethyl sulfide, [illegible] the following constants, which are appreciably different from those cited by us, are given: b.p. 268-272°; n^{20}_D 1.4580; d^{20}_4 0.9216. For the complex compound 1-$C_{12}H_{26}O_2S\cdot HgCl_2$ the obviously erroneous m.p. of 71° is given. This lack of agreement must be attributed to the incomplete purity of the products obtained by the author, who in studying the action of zinc dust on β,β'-chloroethyl sulfide in alcohol obtained a complex mixture of products, which he separated further merely by the method of simple fractionation at ordinary pressure.

2) α,β-Diisobutoxydiethyl Sulfide



$$CH_3-CH\begin{cases} SCH_2CH_2OC_4H_{9i} \\ OC_4H_{9i} \end{cases}$$

(II)

is a colorless liquid having a sharp odor; m.p. 103-105° at 3.5-4 mm; n^{20}_D 1.4486; d^{20}_4 0.9077; found MR_D 69.21; calculated MR_D 68.88.

Found %: C 61.41; 61.33; H 11.23; 12.15; S 13.77; 13.48
$C_{12}H_{26}O_2S$. Calculated %: C 61.49; H 11.18; S 13.68

(a) Reaction of an alcoholic solution of mercuric chloride with the sulfide II gives, in accordance with Equation 1, quantitative separation of hydrochloric acid and the alkoxyethylmercaptomercuric chloride.

Found: α,β-isomer (II) 97.7; 97.9 %.

The precipitated white β-isobutoxyethylmercaptomercuric chloride was obtained by repeated recrystallization from large amounts of boiling alcohol in the form of white tabular crystals, m.p. 144°.

Found %: Cl 9.50; 9.39; S 8.68; 8.60
$C_6H_{13}OSHgCl$. Calculated %: Cl 9.60; S 8.68

(b) Disproportionation of α,β-diisobutoxydiethyl sulfide (II). The sulfide II (11.5 g) and 27% HCl (1 ml) in dioxane were heated in a sealed tube on a boiling water bath for 12 hrs.

After two distillations, the following fractions were obtained:

Fraction 1, 42-43° at 3.5 mm – 3.8 g; n^{20}_D 1.4046
Fraction 2, 50-103° at 3.5 mm – 0.9 g; n^{20}_D 1.4580
Fraction 3, 155-159° at 3 mm – 5.7 g; n^{20}_D 1.4791

Fraction 1, after treatment with metallic sodium and repeated fractionation was found to be diisobutyl acetal (VII), b.p. 42-43° at 3.5 mm; b.p. 170° at 760 mm; n^{20}_D 1.4022; d^{20}_4 0.8180; found MR_D 51.90; calculated MR_D 51.67. [6] m.p. 168-170°; sp.gr. 0.816 at 22°. The bisulfite method of analysis [7] (with addition of H_2SO_4) gave for acetal: 99.1; 99.3%.

Fraction 3 was found to be bis(β-isobutoxyethyl) mercaptal (IX) and had the following constants after repeated fractionation: b.p. 152-154° at 2.7 mm; n^{20}_D 1.4798; d^{20}_4 0.9685; found MR_D 86.36; calculated MR_D 86.04.

Found %: C 56.84; 57.01; H 10.30; 10.34; S 21.84; 21.55
$C_{14}H_{30}O_2S_2$. Calculated %: C 57.09; H 10.27; S 21.77

(c) Action of mercuric chloride on bis(β-isobutoxyethyl) mercaptal (IX) (equation 3). A 20% alcoholic solution of mercuric chloride (6 ml) was added to the mercaptal IX (0.55 g). A finely crystalline white precipitate of β-isobutoxyethylmercaptomercuric chloride (V) formed quickly. The precipitate, after being washed with cold alcohol and dried in a vacuum desiccator, weighed 1.5 g (against theoretical 1.4 g). After being recrystallized twice from hot alcohol, the precipitate melted at 144° and was undepressed in m.p. when mixed with β-isobutoxyethylmercaptomercuric chloride (obtained from the α,β-sulfide II).

3. Action of Hydrogen Sulfide on Isoamyl Vinyl Ether

(a) 55 g of the ether, 0.2 ml of catalyst (0.098% by wt. on the ether of HCl). The experiment was carried out for 7 hrs at room temperature and 12 hrs at 43-45°. The total increase in weight of the reaction mass was 8 g. There were obtained on distillation:

Fraction 1, 30-34° at 5-4.5 mm – 1.1 g; n_D^{20} 1.4168

Fraction 2, 49-50° at 4 mm – 0.9 g; n_D^{20} 1.4458

Fraction 3, 75-125° at 4 mm – 0.8 g; n_D^{20} 1.4573

Fraction 4, 127-134° at 3 mm – 49.7 g; n_D^{20} 1.4560

Fraction 5, 160-175° at 3 mm – 3.8 g; n_D^{20} 1.4670

Amount of α,β-isomer (IV) in mixture: 33.7; 33.7%. Yield of fraction 4 (mixture of the sulfides) 83.8%.

(b) 35 g of the ether, 0.5 ml of catalyst (0.39% by wt of HCl). The experiment was carried out at room temperature (19°). After 5.5 hr the temperature of the reaction mixture reached 26°, and absorption of hydrogen sulfide started suddenly. The experiment lasted for 13 hrs. Increase in weight, 4.5 g. The residue after the unchanged ether (2.4 g) had been driven off was fractionated:

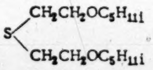
Fraction 1, 35-45° at 2-2.2 mm – 1.2 g
Fraction 2, 90-122° at 2 mm – 1.4 g
Fraction 3, 125-134° at 2 mm – 30.5 g; n_D^{20} 1.4530

Amount of α,β-isomer (IV) in the mixture: 61.1; 61.2%. Yield of fraction 3 (mixture of the sulfides) 81.9%.

4. Properties of the Isomeric Diisoamyloxy Derivatives of Diethyl Sulfide (III) and (IV)

Separation of the mixture of isomers was carried out, as in the previous case, by vacuum distillation through an efficient column. As these substances have high viscosities, the fractionating process was rendered difficult, and the α,β-isomer (IV) was consequently isolated in an insufficiently pure form.

1) β,β'-Diisoamyloxydiethyl Sulfide



$$S\begin{cases}CH_2CH_2OC_5H_{11}i\\CH_2CH_2OC_5H_{11}i\end{cases}$$

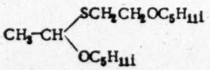
(III)

does not give an acid reaction on addition of an alcoholic solution of mercuric chloride; b.p. 130.2-131° at 2.6-2.8 mm; n_D^{20} 1.4552; d_4^{20} 0.9090; found MR_D 78.4; calculated MR_D 78.1.

Found %: C 64.49; 64.39; H 11.61; 11.65; S 12.44; 12.25
$C_{14}H_{30}O_2S$. Calculated %: C 64.05; H 11.53; S 12.22

Gives a liquid complex compound with mercuric chloride. For this sulfide the literature gives b.p. 191-192 at 33 mm [5].

2) α,β-Diisoamyloxydiethyl Sulfide



$$CH_3{-}CH\begin{cases}SCH_2CH_2OC_5H_{11}i\\OC_5H_{11}i\end{cases}$$

(IV)

b.p. 102-104° at 1.7 mm; n_D^{20} 1.4533; d_4^{20} 0.9052; found MR_D 78.41; calculated MR_D 78.11.

Found %: C 63.87; 63.77; H 11.47; 11.43; S 11.99; 12.10
$C_{14}H_{30}O_2S$. Calculated %: C 64.05; H 11.53; S 12.22

The sulfide (IV) decomposes when it is treated with an alcoholic solution of mercuric chloride with formation of β-isoamyloxyethylmercaptomercuric chloride and with separation of HCl (in accordance with Equation 1).

Content found of α,β-isomer (IV) 91.9; 91.4%.

After being recrystallized twice from hot alcohol, the mercury derivative VI melted at 124.5-125°.

Found %: Cl 9.13; 9.28; S 8.33; 8.11
$C_7H_{15}OSHgCl$. Calculated %: Cl 9.25; S 8.36

In order to bring about its disproportionation, the sulfide (IV) (10 g) was heated in presence of 27.6% HCl (1 ml) in dioxane for 12 hrs on a boiling water bath. The tube was opened and the reaction product diluted with ether. It was washed four times with water in a separating funnel (to remove acid) and then dried. The ether was removed, and the reaction product was vacuum-fractionated:

Fraction 1, 28-29° at 3 mm – 1.6 g
Fraction 2, 66-69° at 3 mm – 1.6 g
Fraction 3, 160-170° at 3 mm – 6.1 g

Isoamyl alcohol was isolated from Fraction 1. From Fraction 2, after a second fractionation, there was separated diisoamyl acetal (VIII); b.p. 66-67° at 3 mm; n_D^{20} 1.4158; d_4^{20} 0.8358; found MR_D 60.72; calculated MR_D 60.90. [8]: b.p. 210.8° (760 mm); sp.gr. 0.8347 at 15°. Fraction 3 was bis(β-isoamyloxyethyl) mercaptal (X). After two fractionations it had the following constants: b.p. 172-175°/3.2 mm; n_D^{20} 1.4800; d_4^{20} 0.9569; found MR_D 95.76; calculated MR_D 95.31.

Found %: C 59.65; 59.49; H 10.72; 10.63; S 19.72; 19.79
$C_{16}H_{34}O_2S_2$. Calculated %: C 59.57; H 10.63; S 19.88

From the β,β'-diisoamyloxydiethylmercaptal (X) obtained by the action of an alcoholic solution of mercuric chloride, there was obtained, in accordance with equation 3, isoamyloxyethylmercaptomercuric chloride (VI). After two recrystallizations it melted at 125° and was undepressed in m.p. when mixed with isoamyloxyethylmercaptomercuric chloride obtained from the sulfide (IV).

SUMMARY

1. It has been shown that addition of hydrogen sulfide to isobutyl vinyl and isoamyl vinyl ethers in dioxane in presence of HCl under conditions similar to those previously described for other vinyl ethers again results in the formation of mixtures of α,β- and β,β'-dialkoxy derivatives of diethyl sulfide.

2. A study has been made of certain chemical reactions of new homologs in the series of dialkoxydiethyl sulfides and β,β'-dialkoxydiethyl mercaptals.

Received July 3, 1951

Institute of Organic Chemistry of the
USSR Academy of Sciences

LITERATURE CITED

[1] E. N. Prilezhaeva, E. S. Shapiro, and M. F. Shostakovsky. Bull. Acad. Sci. USSR. Div. Chem. Sci. 4, 438 (1951).

[2] B. Holmberg, J. prak. Chem. 135, 61 (1932).

[3] E. N. Prilezhaeva, E. S. Shapiro, and M. F. Shostakovsky. Bull. Acad. Sci. USSR. Div. Chem. Sci. 5, 560 (1951).

[4] D. S. Tarbell and D. P. Harnish, Chem. Rev. 49, 67 (1951).

[5] A. E. Kretov. J. Russ. Phys. Chem. Soc., 61, 2345 (1929).

[6] L. de Girard, J. 1880, 695; Ad. Claus, and E. Trainer, Ber. 19, 3008 (1886).

[7] N. A. Gerstein and M. F. Shostakovsky. J. Gen. Chem. 18, 1989 (1948).

[8] M. Alsberg, J. 1864, 485; Ad. Claus and E. Trainer, Ber. 19, 3008 (1886).

SYNTHESIS OF THE VINYL ETHERS OF HIGHER FATTY ALCOHOLS

M. F. Shostakovsky, B. I. Mikhantyev, and V. A. Neterman

The Favorsky-Shostakovsky method [1] for the vinylation of alcohols has received general recognition and wide application in laboratory practice and in industrial production. The great interest aroused by vinyl ethers has brought the question of the vinylation of higher fatty alcohols into prominence. The sporadic data concerning a few alkyl vinyl ethers that is to be found in the foreign patent literature and the isolated facts in our own literature do not present a complete picture of these compounds.

In order to make a study of the general and individual properties of these ethers, the vinylation of the following fatty alcohols was undertaken: hexyl, cyclohexyl, heptyl, octyl, iso-octyl, nonyl, and decyl (see Table 1).

TABLE 1

Characteristics of Alcohols Used

Name and Formula	B.p. °C/760 mm	n_D^{28}
Hexyl alcohol $C_6H_{13}OH$	157	1.4181
Heptyl alcohol $C_7H_{15}OH$	175-176	1.4228
Octyl alcohol $C_8H_{17}OH$	196	1.4290
Iso-octyl alcohol $C_6H_{13}CHOHCH_3$	179-180	1.4275
Nonyl alcohol $C_9H_{19}OH$	214-215	1.4363
Decyl alcohol $C_{10}H_{21}OH$	231	1.4370
Cyclohexyl $C_6H_{11}OH$	160.7	1.4645

It was found that vinylation of higher fatty alcohols exhibits certain peculiarities. The vinylation process proceeds more slowly than for the C_1–C_5 alcohols. At 140-160°, only 72-80% of the theoretically necessary acetylene is absorbed (Fig.1). When the temperature is then raised to 180°, 90-96% of acetylene is absorbed, depending on the complexity of the alcohol used. Further raising of the temperature causes secondary feactions.

The rate of vinylation depends on the initial pressure of acetylene (Fig.2). For an initial pressure of 17-18 atm the time required for vinylation of 3 mole of alcohol is 2.5 hrs less than for 12-13 atm initial pressure. Hexyl alcohol vinylates more rapidly than octyl alcohol. Iso- and cyclic alcohols vinylate somewhat more slowly than the corresponding normal alcohols. Also, the purification of the ethers is complicated. The washing-out of the alcohols, as applied to the purification of the C_3–C_5 ethers [2], is not applicable in the present case, since the higher alcohols are practically insoluble in water. The alcohol forms an azeotrope with the vinyl ether, and fractional distillation is of no value. Four or five repetitions of a process consisting in treatment of the vinyl ethers with metallic sodium followed by vacuum distillation from a Favorsky flask and a final fractionation through a column enable pure preparations to be obtained with a yield of 80.4-89.2% (see Table 2). Generally speaking, the yields of the vinyl ethers of higher fatty alcohols are not cited in the foreign literature.

We have established that better results are obtained by carrying out the vinylation of higher fatty alcohols at 140-180° rather than at lower temperatures.

In a review article by Schildknecht and others [3] corrected physical constants are cited for vinyl ethers. However, the boiling points

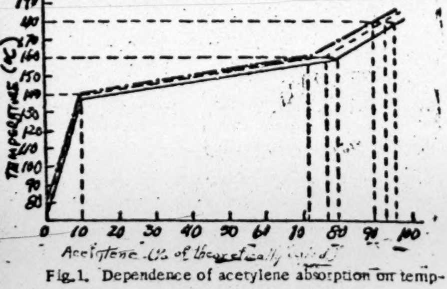


Fig.1. Dependence of acetylene absorption on temperature: -.-.- nonyl and decyl alcohols; —— octyl and iso-octyl alcohols; – – – hexyl, heptyl, and cyclohexyl alcohols

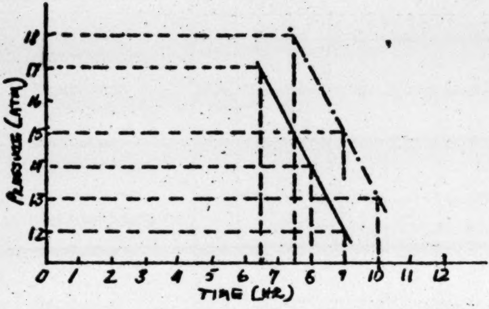


Fig. 2. Dependence of time required for vinylation on complexity of alcohol and on initial pressure:- _ . _ . iso-octyl alcohol; —hexyl alcohol. NOTE: 3 mole of alcohol was taken.

of the octyl and decyl ethers are given for reduced pressure (4 and 10 mm), i.e. there is no possibility of following the regular rise in the boiling points of the ethers associated with increasing complexity of the radicals or of deciding the important question of the stability of the ethers to heat. The investigations have shown that the C_8–C_{12} alkyl vinyl ethers can be distilled at ordinary pressure without decomposition. The ethers have lower boiling points than the corresponding alcohols, and they are more mobile. When kept for a long time (6 months or more), the ethers become slightly yellow and partially hydrolyzed. Hydrolysis, of course, is one of the methods for the establishment of the structure and of the purity of alkyl vinyl ethers. Hydrolysis of hexyl vinyl and iso-octyl vinyl ethers (0.15 mole) by means of 5% aqueous sulfuric acid at 70-80° for 3-4 hrs showed that they are completely decomposed into aldehyde and alcohol. The products obtained were characterized by their physical constants.

As will be seen from Table 2, the sp.gr., refractive index, and molecular refraction increase in regular fashion with increase in the molecular weight of the ether in accordance with generally held ideas concerning this homologous series. The experimentally determined molecular weights and the analyses for carbon and hydrogen confirm the purity of the compounds synthesized.

EXPERIMENTAL

We will take as example the vinylation of hexyl alcohol (b.p. 157.8°; n_D^{20} 1.4181). The vinylation was carried out in a 2.6-liter autoclave. The alcohol (306.0 g, 3 mole) and KOH (24 g) were introduced into the autoclave, and acetylene was passed in under a pressure of 18 atm at 26°. The heat was switched on, and the autoclave was set in rotation; the pressure rose to 20-21 atm, but at 140-160° it began to fall. The first two portions of acetylene were fully absorbed, but the next was absorbed only to the extent of 40-70%. When 70-80% of the theoretically calculated amount of acetylene had been absorbed, the rate of absorption fell sharply. In order to intensify the process, the temperature was raised to 180°, thus permitting absorption of acetylene to proceed up to 93-96% of the theoretically possible amount.

When the autoclave had cooled, the residual acetylene was allowed to escape, and the reaction mixture was removed, the autoclave being rinsed out with ether. After standing, the brown reaction mixture separated out into two layers, a liquid upper layer, and a thick, viscous lower layer. The liquid layer was poured off and fractionally distilled; the lower layer was extracted with ether, three or four treatments being required to complete the extraction of organic substances. The extraction is important in order to increase the yield of the vinyl ether. The ether extract was united with the ethereal washings from the autoclave and then distilled.

The crude vinyl ether was treated five times with metallic sodium, and after each treatment it was distilled from a Favorsky flask. Finally, it was distilled through a column of 15-16 theoretical plates having a glass filling. Altogether 342.5 g (89.2%) of a pure preparation was obtained.

Hydrolysis

A mixture consisting of hexyl vinyl ether (19.2 g, 0.15 mole) and 0.1 N H_2SO_4 (15 ml) was placed in a flask fitted with mechanical stirrer and reflux condenser and was heated for 3 hrs at 70-80° on the water-bath. Acetaldehyde was collected in a coil trap connected to the condenser and cooled to −45° by means of solid carbon dioxide in acetone. The yield of acetaldehyde was 6.00 g (91%), and 15 g (98%) of hexyl alcohol was

BLANK
PAGE

TABLE 2

Physical Properties of Alkyl Vinyl Ethers

Name and Formula	Yield %	B.p. °C/760 mm	d_4^{20}	n_D^{20}	MR_D		M		% C		% H	
					found	calcd.	found	calcd.	found	calcd	found	calcd.
Hexyl ether • $H_2C{=}CHOC_6H_{13}$	89.2	143.5	0.7970	1.4171	40.461	40.480	127.28	128.208	74.85	74.94	12.65	12.58
Heptyl ether $H_2C{=}CHOC_7H_{15}$	85.1	165.5-166.0	0.8021	1.4220	45.061	45.118	141.95	142.234	75.88	75.99	12.83	12.76
Octyl ether $H_2C{=}CHOC_8H_{17}$	85.0	186.0-187.0	0.8028	1.4270	49.974	49.756	156.07	156.260	76.92	76.85	13.15	12.90
Iso-octyl ether $H_2C{=}CHOC_8H_{17}$-iso	84.3	175.2-176.2	0.8019	1.4263	49.959	49.756	155.41	156.260	76.40	76.85	12.90	12.90
Nonyl ether• $H_2C{=}CHOC_9H_{19}$	80.4	206.1-207.0	0.8089	1.4310	54.421	54.394	170.85	170.286	77.40	77.58	13.11	13.02
Decyl ether• $H_2C{=}CHOC_{10}H_{21}$	80.5	224.2-225.0	0.8123	1.4347	59.172	59.032	184.04	184.312	78.14	78.19	13.20	13.13
Cyclohexyl ether•• $H_2C{=}CHOC_6H_{11}$-cyclo	86.9	147.4-148.0	0.8883	1.4546	38.514	38.260	126.60	126.192	76.18	76.14	11.07	11.18

• Described for the first time

•• Polymerized by heat

obtained; both compounds were characterized by their physical constants (aldehyde, b.p. 20.3°; n_D^{10} 1.3332; alcohol, b.p. 158°; n_D^{20} 1.4181).

SUMMARY

1. A study has been made of the vinylation of the C_6–C_{10} fatty alcohols.
2. The C_8–C_{12} vinyl ethers have been obtained in yields of 80.4-89.2 %.
3. The synthesized vinyl ethers have been characterized by their physical constants.

Received October 21, 1951

Institute of Organic Chemistry of the
USSR Academy of Sciences

LITERATURE CITED

[1] A. E. Favorsky and M. F. Shostakovsky. Author's Cert. No. 26950 of March 13, 1940.

[2] A. E. Favorsky and M. F. Shostakovsky. J. Gen. Chem. 13, 1-2, 1 (1943).

[3]. C. E. Schildknecht et al. Ind. Eng. Chem. 39, 180-186 (1947).

BLANK
PAGE

DESULFURIZING ACTION OF TROSHKOV KAOLIN

E. A. Timofeeva, N. I. Shuikin, and V. M. Kleimenova

Although there is a wide literature on the desulfurization of motor fuels, the problem of desulfurization is not yet fully solved. This question, however, is assuming increasing importance now that manufacturing and processing concerns are being supplied with considerable quantities of sulfur-containing petroleums and with tars, containing various amounts of sulfur, derived from coal, shale, and sapropelites. As is well known, sulfur compounds cause corrosion and formation of deposits in engines; they adversely affect the antidetonation characteristics of the fuel, reduce its sensitivity to tetraethyl-lead, and produce a number of other undesirable phenomena. The permitted limit of sulfur in automobile gasolines is 0.15%; the limit for gasolines obtained from sulfur-containing petroleums is 0.4-0.6%. It is necessary, however, to aim at a considerable reduction in these upper limits.

Thus, Semenov [1], investigating the effect of the sulfur content of the gasoline on the functioning of the engine, found that an increase in the sulfur content of the gasoline from 0.05 to 0.6% reduces the power and efficiency of the engine by 25-35% and its service life by at least a quarter. He considers that it is essential to reduce the content of sulfur in gasolines to 0.05-0.07%.

In the present work we have investigated the use of Troshkov kaolin as a desulfurizing agent. As shown in our previous investigations, this kaolin may be used as starting material for the preparation of a good refining catalyst for the treatment of certain fractions of the primary tar from Budagov sapropelites. In order to study its desulfurizing propensity, the Troshkov clay was applied to the treatment of sulfur-containing direct-distillate gasolines and also of desulfurized gasoline to which additions of particular sulfur compounds had been made.

EXPERIMENTAL

The catalyst was prepared from clay that had not been activated with acid. Desulfurization was carried out at atmospheric pressure in the usual flow-type apparatus used for catalysis work. The temperature was measured by means of a thermocouple. Gasoline was passed at a space velocity of 0.3. Before the experiment the furnace was heated to the necessary temperature and air was blown through the catalyst tube in order to dehydrate the catalyst more fully. At the end of the experiment the catalyzate was washed with 10% caustic soda (to remove the hydrogen sulfide formed) and with water. It was then dried with calcium chloride and weighed, and determinations were then made of sulfur ("lamp method"), refractive index, specific gravity, and amount of sulfonatable hydrocarbons.

The original gasoline D, the variety that we used for the most part in our study of the desulfurizing action of Troshkov kaolin, had the following properties: d_4^{20} 0.7390; n_D^{20} 1.4193; sulfur content 0.185%; iodine no. 2.2; sulfonatable hydrocarbons 10% by vol.

Fractional Composition

Commencement of boil	64°	60 % by vol.	141°
10 % by vol.	84°	70 "	153°
20 "	95°	80 "	165°
30 "	107°	90 "	180°
40 "	118°	95 "	192°
50 "	130°	98 "	200°
		2 "	residue + loss

First of all the effect of temperature on the degree of desulfurization of the gasoline was determined. For this purpose 30 ml of catalyst was taken in a catalysis tube of internal diameter 10 mm. In each experiment gasoline was passed in 30 ml portions. Experiments were carried out at 50° intervals from 200 to 500°. The results obtained are given in Table 1.

On the basis of the results obtained we considered the optimum desulfurization temperature to be 400°.

TABLE 1

Effect of Temperature on the Degree of Desulfurization of Gasoline

Gasoline	Temp. of expt. (°C)	n_D^{20}	d_4^{20}	Sulfonatable content, %	Sulfur content, %	Iodine No.
Original gasoline D	—	1.4193	0.7390	10.0	0.185	2.2
Catalyzate	200	1.4160	0.7404	—	0.101	3.6
"	250	1.4165	0.7400	—	0.073	2.9
"	300	1.4170	0.7400	—	0.067	3.0
"	350	1.4168	0.7393	10.0	0.048	2.6
"	400	1.4160	0.7400	11.0	0.031	2.1
"	450	1.4184	0.7406	18.0	0.032	2.0
"	500	1.4190	0.7410	30.0	0.033	2.2

The sulfur content of the gasoline was reduced at this temperature from 0.185 to 0.031%. However, on raising the temperature the degree of desulfurization did not alter (see Table 1). In order to compare thermal and catalytic desulfurization of gasoline, we carried out comparable experiments at 200, 400, and 500° in presence and in absence of catalyst (in the latter case some glass wool was placed in the catalysis tube).

The results in Table 2 show that under these conditions of temperature thermal treatment of gasoline D gives a considerably lower degree of desulfurization than catalytic treatment.

In order to determine the stability of the catalyst and the possibility of its regeneration, prolonged experiments were carried out on the catalytic treatment of gasoline D with Troshkov clay at 400°. The experimental conditions were: 100 ml (74.1 g) of catalyst (length of layer, 62 cm), in a catalysis tube 1.6 cm in diameter; gasoline passed in 100 ml portions; 40 experiments in all. After the passage of 1000 ml of gasoline, the catalyst was regenerated by passing air through it at 500° for 3 hrs 20 min (duration of experiment). The results obtained are given in Table 3.

TABLE 2

Comparative Experiments on the Desulfurization of Gasoline D in presence of Troshkov Clay and of Glass Wool

Gasoline		Temp. of expt. (°C)	n_D^{20}	d_4^{20}	Sulfonatable content, %	Sulfur content, %	Iodine No.
Original gasoline D		—	1.4193	0.7390	10.0	0.185	2.2
Condensate obtained in presence of	clay	200	1.4160	0.7404	—	0.101	3.6
	glass wool	200	1.4150	0.7439	—	0.172	3.2
	clay	400	1.4160	0.7400	11.0	0.031	2.1
	glass wool	400	1.4160	0.7438	11.0	0.126	7.7
	clay	500	1.4190	0.7410	30.0	0.033	2.2
	glass wool	500	1.4145	0.7403	13.5	0.097	8.2

Altogether, the catalyst was in work for 133 hrs 20 min, during which time it was regenerated three times. As will be seen from the results in Table 3, its desulfurizing activity did not change. The yield of catalyzate, washed with alkali and dried with calcium chloride, was about 97%.

In each passage of a 100 ml portion of gasoline over the clay, on the average 450 ml of gas was evolved. This gas had the following composition:

Unsaturated substances	10.5%
Hydrogen	55.8%
Oxygen	0.5%
Methane hydrocarbons	32.0%
Nitrogen	1.2%

As will be seen from the results, the sulfur content of catalyzates obtained by passage of the gasoline over fresh catalyst that has not been regenerated (the first 10 experiments) is reduced in comparison with that of the original gasoline by a factor of 5 or 6. The regenerated catalyst, on the other hand, carries the desulfurization much further: in the catalyzates of experiments 15, 16, and 21 the sulfur content is reduced by a factor of 18. The phenomenon of increased activity in aluminum silicate catalysts after regeneration has been noted also in cracking reactions [2]. The combined catalyzate had the following properties: n_D^{20} 1.4185; d_4^{20} 0.7335; sulfonatables 11.0% by vol; 0.018% S; iodine No. 2.1.

TABLE 3

Variation in Catalyst Activity in the Desulfurization of Gasoline D at a Space Velocity of 0.3 at 400°

Expt. No.	n_D^{20}	Sulfur content %	Expt. No.	n_D^{20}	Sulfur content, %
Original gasoline	1.4193	0.185	Regeneration		
1	1.4160	0.031			
5	1.4155	0.041	21	1.4151	0.011
6	1.4148	0.041	26	1.4155	0.036
10	1.4160	0.037	30	1.4163	0.031
Regeneration			Regeneration		
11	1.4150	0.016	31	1.4150	0.014
15	1.4185	0.010	36	1.4160	0.022
16	1.4156	0.012	40	1.4161	0.030
20	1.4150	0.030			

Fractional Composition

Commencement of boil	60.0°	70 % by vol.	154.0°
10 % by vol.	81.0°	80 "	164.5°
20 "	90.5°	90 "	180.0°
30 "	105.5°	95 "	193.0°
40 "	117.0°	98 "	200.0°
50 "	129.0°	2 "	residue + loss
60 "	141.8°		

TABLE 4

Variation in the Activity of Thermally Activated Catalyst in the Desulfurization of Gasoline

Expt. No.	n_D^{20}	Sulfur content, %
1	1.4185	0.011
6	1.4185	0.018
11	1.4180	0.028
16	1.4170	0.028
21	1.4157	0.035
26	1.4200	0.045
31	1.4220	0.056
36	1.4152	0.059
41	1.4162	0.060
Regeneration		
42	1.4148	0.012

Thus, as a result of the catalytic treatment of the original gasoline D with Troshkov clay at 400°, the sulfur content of the gasoline is reduced by a factor of 10.

The fractional composition of the gasoline obtained is altered somewhat in the "light" direction, as compared with the original gasoline. It is important to note that the process is accompanied by inappreciable losses.

It was of interest to discover whether the great increase in the desulfurizing propensity of the clay caused by regeneration (see Table 3) depends only on thermal action, or whether some other factors are concerned. With this in view, a portion of fresh catalyst (30 ml, 22.9 g; tube diameter 10 mm; length of catalyst layer 160 mm) was heated in a stream of air under the conditions of the regeneration. Gasoline D (30 ml) was then passed over the catalyst at 400° at a space velocity of 0.3. The sulfur content of the gasoline fell to 0.011% (see expt. 1 in Table 4). Without thermal activation of the catalyst, the sulfur content of the gasoline fell to 0.031% (see expt. 1, Table 3). Thus, prior thermal treatment of the clay increases its desulfurizing propensity by a factor of approximately 3.

A further 40 portions of gasoline were passed over the same catalyst before it was regenerated. The results are given in Table 4.

The results given in Table 4 show that the desulfurizing propensity of the catalyst is preserved for a fairly long time, although it does fall in time. After working for 136 hrs 40 min. the catalyst reduces the sulfur content of the gasoline by a factor of 3 (expt. 41, Table 4). The subsequent regeneration of the catalyst leads to the complete recovery of its original activity (expt. 42, Table 4).

We have carried out desulfurization experiments also on two other gasolines: gasolines B and K. The catalyst employed for the desulfurization of gasoline D was used after regeneration, and the conditions of the experiment were as before (400°, space velocity 0.3).

The results of the experiments are shown in Table 5.

Thus, also for these gasolines Troshkov clay is a good desulfurizing catalyst.

TABLE 5

Desulfurization of Gasolines B and K in Presence of Troshkov Clay

Gasoline	n_D^{20}	d_4^{20}	Sulfonatables, % by vol.	Sulfur content, %
Original B	1.4153	0.7484	9.0	0.030
Catalyzate	1.4173	0.7488	9.0	0.007
Original K	1.4178	0.7490	6.0	0.018
Catalyzate	1.4172	0.7551	7.0	0.003

In order to elucidate the effect of the nature of the sulfur-containing compounds on the desulfurization process, we carried out experiments on purified gasoline to which additions of particular sulfur compounds had been made. Gasoline D treated carefully with 3% oleum had the following properties; n_D^{20} 1.4105; d_4^{20} 0.7335; sulfur content 0.003%. To this gasoline, additions were made of propanethiol, thiophene, tetrahydrothiophene, or diisopentyl sulfide so as to give a calculated sulfur content of about 0.2%. Determinations were made of the sulfur contents and refractive indices of these mixtures. The samples obtained were passed in 30 ml portions under the same conditions over the same volume of catalyst; some samples were passed twice in succession. When each new sample had been treated catalytically with the clay, the catalyst was regenerated. The properties of the original mixtures and of the catalyzates are given in Table 6.

TABLE 6

Results of Desulfurization Experiments on Gasoline Containing Particular Sulfur-containing Compounds

Gasoline	n_D^{20}	Sulfur Content %	Notes
Purified gasoline + propanethiol	1.4110	0.180	—
Catalyzate	1.4115	0.007	Odor of hydrogen sulfide in catalyzate
Purified gasoline + thiophene	1.4110	0.203	—
Catalyzate	—	0.138	—
Catalyzate after a second passage	1.4135	0.133	—
Purified gasoline + tetrahydrothiophene	1.4108	0.209	—
Catalyzate	—	0.146	—
Catalyzate after a second passage	1.4140	0.063	—
Purified gasoline + diisopentyl sulfide	1.4112	0.193	—
Catalyzate	—	0.047	Odor of hydrogen sulfide in catalyzate
Catalyzate after a second passage	1.4169	None	Ditto

Thus, a catalyst prepared from Troshkov clay effects almost complete removal from gasoline of sulfur present as mercaptan (96.0%) or as thio-ether (after a double passage). A single passage removes 30% of tetrahydrothiophene sulfur, a double passage removes 70%. The question of the removal of thiophene sulfur is a more complicated one: catalytic treatment of the sample of thiophene-containing gasoline removes only about 34% of the sulfur present, and a second operation has no appreciable effect.

SUMMARY

1. An investigation has been made into the desulfurizing action of Troshkov kaolin on three samples of sulfur-containing gasolines and on mixtures of purified gasoline with propanedithiol, with diisopentyl sulfide, with thiophene, and with tetrahydrothiophene.

2. It has been shown that a catalyst prepared from unactivated Troshkov clay has a high desulfurizing propensity at 400°.

3. It has been found that thermal activation of the clay increases its desulfurizing activity by a factor of about 3.

4. Troshkov clay removes from gasoline not only aliphatic sulfur-containing compounds (mercaptans, thio-ethers), but also cyclic sulfur compounds (tetrahydrothiophene).

Received October 26, 1951

Institute of Organic Chemistry of the
USSR Academy of Sciences

LITERATURE CITED

[1] N. Semenov. The Automobile, No. 2, 12 (1950).

[2] G. L. Lyubarsky and M. P. Kozina. Problems in Kinetics and Catalysis. VI. Heterogeneous Catalysis. USSR. Acad. Sci. Press. Moscow and Leningrad. 1949.

CATALYTIC ALKYLATION OF AMMONIA WITH HALOGEN DERIVATIVES OF ALKANES AND CYCLOALKANES

COMMUNICATION 1

V. A. Nekrasova and N. I. Shuikin

There is no information in the literature concerning the catalytic alkylation of ammonia in the vapor phase by means of alkyl and cycloalkyl halides. There are, however, a number of investigations on the synthesis of amines by the action of liquid ammonia on certain organic halogen compounds [1]. Work with liquid ammonia is, of course, carried out under pressure in autoclaves, a process that is attended by considerable difficulties. We therefore set ourselves the task of studying the conditions required for the catalytic synthesis of amines of the aliphatic and alicyclic series in a continuous-flow system under ordinary pressure. The vapor-phase method for the catalytic synthesis of amines at atmospheric pressure has great possibilities for the production of these important substances and will be of great value for the further development of the chemistry and technology of amines. As a result of our investigations we have succeeded in finding a suitable catalyst, based on magnesium oxide, which, under suitable conditions, promotes the catalytic synthesis of amines in high yield from alkyl halides.

EXPERIMENTAL

In the selection of catalysts information in the literature on the amination of alcohols and of alkenes was taken into account. However, the most active catalysts for the amination of alcohols (platinized silica gel, etc.) [2] were found to be unsuitable for our purpose; the yield of amine was low when they were used, and at the same time splitting-off of halogen halide with formation of unsaturated hydrocarbons occurred to an appreciable extent. In view of the latter circumstance, it was decided that in further work catalysts employed for the amination of alkenes should be used so that in the moment of formation unsaturated hydrocarbons should be converted into amines.

Teter [3] alkylated ammonia with alkenes in presence of reduced oxides of cobalt and nickel deposited on bentonite that had been treated with acid. As catalysts we tried reduced nickel and cobalt, also their hydroxides and halides on asbestos, charcoal, pumice, kieselguhr, and silica gel. However, they were all found to be unsuitable, for the undesired formation of unsaturated hydrocarbons was found to occur in their presence.

After lengthy investigations we found that amination of the halogen compounds proceeds with a good yield of amines in presence of a catalyst based on magnesium oxide. This catalyst retains its activity for 3.5 hrs., after which it can be regenerated by heating in air to dull red heat or by oxidation with pure air at 350° in the reaction tube itself. Experiments were carried out with 1-chlorobutane, 1-chlorohexane, 1-chloroheptane, 1-chloro-octane, 1-chlorononane, 1-chlorodecane, chlorocyclopentane, chlorocyclohexane, and bromocyclohexane. The properties of the halogen compounds taken for investigation are given in Table 1.

The halogen compounds were introduced by means of an automatic buret into a silica flask, into which gaseous ammonia was passed simultaneously. The flask was heated on an oil bath. The mixture of vapors was directed into a glass tube containing catalyst; the tube was situated in an electric furnace fitted with a thermoregulator. The volume of catalyst was 100 ml in all experiments; the molecular ratio of ammonia and halogen derivative was 2:1; the space velocity was taken to be 0.2 in all experiments. The reaction products were collected in a receiver cooled with ice and salt. The condensates obtained were dried by means of anhydrous sodium sulfate and were analyzed for amine-nitrogen content by Francois' method [4]. The estimation of primary amine was carried out by Van Slyke's method [5]. The content of tertiary amine was estimated by treating the mixture of amines with nitrous acid and titrating the amine subsequently distilled off. The amount of secondary amine was found by difference. The gases formed in the reaction were collected in a graduated gasholder and analyzed by the usual method; hydrogen was estimated by Jager's method [6] by combustion over copper oxide.

TABLE 1

Properties of the Alkyl and Cycloalkyl Halides Used

Substance	B.p. * (°C)	n_D^{20}	d_4^{20}
1-Chlorobutane	78.5	1.4015	0.8840
1-Chlorohexane	135.0	1.4230	0.8779
1-Chloroheptane	159.5	1.4292	0.8745
1-Chloro-octane	184.0	1.4325	0.8869
1-Chlorononane	190.0	1.4402	0.8806
1-Chlorodecane	223.0	1.4381	0.8702
Chlorocyclopentane	114.0	1.4497	1.0025
Chlorocyclohexane	142.0	1.4627	0.9987
Bromocyclohexane	163.0	1.4958	1.3241

Of all the catalysts tried, one based on magnesium oxide gave the best results for the alkylation of ammonia by means of the halogen compounds taken for investigation (see Tables 2 and 3). Low yields were obtained in presence of the other catalysts tried.

SUMMARY

1. The catalytic alkylation of ammonia in the gas phase at ordinary pressure has been carried out with good yields by means of halogen derivatives of alkanes and cycloalkanes.

2. Of various catalytic agents tried, the most effective was found to be a catalyst prepared from magnesium oxide.

3. The amine contents of the catalyzates obtained in presence of this catalyst at 310° in the reactions between ammonia and chloroalkanes (1-chlorobutane, 1-chlorohexane, 1-chloroheptane, 1-chloro-octane, 1-chlorononane, and 1-chlorodecane) (space velocity 0.2) were 60.0, 60.5, 61.0, 63.0, 77.0, and 78.6% respectively.

TABLE 2

Synthesis of Aliphatic Amines at 310° in Presence of a Catalyst Prepared from Magnesium Oxide

Chloroalkane	Yield of condensate, % of orig. chloroalkane	Amine nitrogen in catalyzate, %	Yield of amine (%)		
			primary	secondary	tertiary
1-Chlorobutane	80.5	11.4	39.2	18.1	2.7
1-Chlorohexane	82.1	12.0	45.0	13.0	2.5
1-Chloroheptane	84.1	11.8	50.5	9.0	1.5
1-Chloro-octane	83.2	10.5	58.0	4.2	0.8
1-Chlorononane	83.5	9.7	69.0	8.0	–
1-Chlorodecane	84.4	8.7	70.6	8.0	–

NOTE. Duration of each experiment: 1 hr.

TABLE 3

Synthesis of Alicyclic Amines at 340° in presence of a Catalyst prepared from Magnesium Oxide

Halogen derivative	Yield of condensate, % of orig. halogen deriv.	Amine nitrogen in catalyzate, %
Chlorocyclopentane	98.1	11.5
Chlorocyclohexane	97.7	10.2
Bromocyclohexane	97.5	9.7

NOTE. Duration of each experiment: 1 hr.

4. The effect has been studied of the length of the carbon chain in alkyl halides on the yield of amines, and it has been shown that with increase of chain length from C_4 to C_{10} the amine content of the catalyzate rises from 60.0 to 78.6%.

5. In presence of the same catalyst at 340° and under otherwise identical conditions, chlorocyclopentane, chlorocyclohexane, and bromocyclohexane yield catalyzates containing 11.5, 10.2 and 9.7% of amine nitrogen respectively.

Received May 9, 1951

Institute of Organic Chemistry
of the USSR Academy of Sciences

LITERATURE CITED

[1] J. Braun, Ber. 70. 979 (1937); J. Wibaut, F. Heiermann and H. Wagtendonk, Rec. trav. chim. Pays-Bas 57, 456 (1938); O. Westphal and D. Jerchel, Ber. 73, 1002 (1940); G. S. Markova and A. I. Shatenshtein. Proc. Acad. Sci. USSR, 35, 73 (1942); N. S. Spasokukotsky, G. S. Markova, and A. I. Shatenshtein. J. Gen. Chem., 15, 42 (1945).

[2] M. A. Popov. J. Gen. Chem., 18, 438, 1109 (1948).

---

*Corrected

[3] J. W. Teter. U.S. Pat. 2417897 and 2417892 of 25/3/1947. U.S. Pat. 2419470 of 22/4/1947; Chem. Abs. 41, 5144 (1947).

[4] M. Francois, Comptes. rend. 144, 567, 857 (1907).

[5] D. D. Van-Slyke, Z. physiol. Chem. 47, 458 (1906).

[6] H. Jager, J. Gasbeleuchtung 41, 764 (1898).

BLANK
PAGE

THE PREPARATION OF STYRENE BY CATALYTIC DEHYDROGENATION OF THE ETHYLCYCLOHEXANE FRACTION OF MAIKOP GASOLINE

N. I. Shuikin and I. I. Levitsky

Catalytic dehydrogenation of ethylbenzene is the most widely used method for the preparation of styrene and is the method that has received the greatest amount of study [1,2]. The reaction occurs at 600-650° in presence of difficultly reducible metal oxides as catalysts. The yield of styrene is greatly increased by diluting the ethylbenzene vapor by, e.g., carbon dioxide, steam, or nitrogen. One of the first investigations in this field was that of Zelinsky and coworkers [3]; in this a study was made of a number of catalysts for the dehydrogenation of ethylbenzene and of the way in which temperature, nature of diluent, degree of dilution, and other factors affected the course of the reaction. These investigations showed that oxide catalysts based on copper-chromium or on vanadium-aluminum are of high activity and are readily regenerated.

The reaction, discovered by Zelinsky, by which cyclohexane and its homologs are dehydrogenated over palladium or platinum black has served as a basis for the development of a new method for the study of the chemical nature of gasolines [4,5,6,7]. This reaction, in which the six-membered cycloalkanes are converted smoothly into the corresponding aromatic hydrocarbons at 300°, is the basis of a well-tried method for the exhaustive catalytic aromatization of gasolines [8]. The oxide catalysts (chromium oxide, vanadium oxide, etc.), also are able to initiate dehydrogenation of cyclohexane hydrocarbons, but the reaction occurs at a higher temperature (450-475°) and is complicated by side-reactions [9].

We considered that it would be interesting to investigate the possibility of extending the method for the dehydrogenation of cycloalkanes to the catalytic synthesis of styrene from the ethylcyclohexane of petroleum. Two methods for this synthesis can be envisaged: a) catalytic aromatization of the ethylcyclohexane fraction of gasoline over platinized charcoal and subsequent dehydrogenation of the ethylbenzene obtained (in admixture with xylenes, alkanes, and five-membered cycloalkanes) over an oxide catalyst, and b) separation of ethylbenzene and of xylenes from the aromatized (300°) ethylcyclohexane fraction and subsequent catalytic dehydrogenation of ethylbenzene. Also a third variant of the synthesis may be pointed out — direct dehydrogenation of the ethylcyclohexane fraction over oxide catalysts to styrene, i.e. simultaneous dehydrogenation of the cyclohexane ring and of the ethyl substituent.

Investigations in this direction have been carried out by one of us in conjunction with Usov and Marukyan [10]; we studied the dehydrogenation of the ethylcyclohexane fraction (127-134°) of Maikop gasoline over a copper-chromium oxide catalyst at 625° in a stream of carbon dioxide. The catalyzates obtained contained 21.0-31.3% of styrene. Dehydrogenation under similar conditions of a previously aromatized (300°) ethylcyclohexane fraction of the same gasoline yielded catalyzates containing 20-25% of styrene. Thus, two variants of the synthesis of styrene from the ethylcyclohexane of petroleum have been explored. The present work constitutes a continuation and development of the above investigation.

The dehydrogenation of the ethylcyclohexane fraction of Maikop gasoline and of the product of its smooth catalytic aromatization at 300° was carried out by us at 575° over a catalyst based on the oxides of vanadium and aluminum. By changing the reaction conditions with respect to those used in the previous work, we endeavored to restrict, as far as possible, destruction of the hydrocarbons. Separation of the ethylcyclohexane fraction of the gasoline was carried out by the aid of a considerably more efficient column. The determination of the combined content of ethylcyclohexane and natural ethylbenzene was carried out by Ullmann's oxidation method. The results of this determination were lower than those obtained in the previous work [10] by the Raman-spectrum method. This divergence is probably due to a difference in chemical composition between the two different samples of Maikop gasoline taken for investigation and also, possibly, to the use of an insufficiently pure ethylbenzene standard.

In the present work we investigated also the third variant of the catalytic synthesis of styrene from the ethylcyclohexane fraction: separation of an ethylbenzene-xylene concentrate followed by its dehydrogenation.

EXPERIMENTAL

Separation of the Ethylcyclohexane Fraction, B.p. 127-134°

For the investigation we took the Maikop straight-distillate gasoline, containing 8% of aromatic hydro-
rbons and characterized by the following constants: boiling limits 41-165°; d_4^{20} 0.7630; n_D^{20} 1.4125. The
ad fraction (up to 103°) of the gasoline was separated by the use of a laboratory column of 7-8 theoretical
ates. The remainder was carefully fractionated through a column of 19 theoretical plates, and the fraction
b.p. 127-134° was separated. This fraction had d_4^{20}. 0.7792; n_D^{20} 1.4341 and contained 26% aromatic
drocarbons.

Aromatization of the Ethylcyclohexane Fraction

The fraction of b.p. 127-134° was aromatized smoothly by passage over platinized charcoal at a space
locity of 0.3* at 300°. The high activity of the catalyst with respect to cyclohexane was characterized by
refractive index of the catalyzate n_D^{20} 1.4945. The catalyzate obtained from the ethylcyclohexane fraction
tained 47% of aromatic hydrocarbons and had n_D^{20} 1.4479 and d_4^{20} 0.7965. A second passage over the catalyst
nged the refractive index only slightly to n_D^{20} 1.4485. Thus, the aromatization of the ethylcyclohexane
ction was almost complete after the first operation.

Determination of the Content of Ethylbenzene in the Catalyzate

The estimation of ethylbenzene was carried out by treatment of the catalyzate with a 5% alkaline
tion of permanganate (which oxidizes the ethylbenzene and xylenes contained in the catalyzate) according
he method described by Moldavsky and coworkers [11], with the modifications introduced by Maslyansky
Berlin [12]. It was found that the distribution of aromatic hydrocarbons in the catalyzate was as follows:
5% of ethylbenzene, 28.4% of o-xylene, and 36.1% of m- and p-xylenes.

The ethylbenzene in the catalyzate consisted of natural ethylbenzene and of the ethylbenzene formed
ehydrogenation of ethyicyclohexane. As noted above, the catalyzate contained 47% of aromatic hydro-
ons. Hence, the combined content of natural ethylbenzene and ethylcyclohexane in the original fraction
so of ethylbenzene in the catalyzate) was (47 x 35.5)/100 = 16.7%. In order to increase the concentration
hylcyclohexane in the fraction, a more efficient column and a narrower distillation-temperature range
ld probably be required; however, separation of a fraction within a range of less than 6-7° leads to incom-
e extraction of ethylcyclohexane from the gasoline.

The lowness of the concentration of ethylcyclohexane in the original fraction and also, therefore, of
lbenzene in the aromatization product from this fraction decided the main course of further work: separation
investigation of an ethylbenzene-xylene concentrate. The second of the dehydrogenation variants referred to
e was therefore taken as the basis of the main line of investigation.

Separation of the Ethylbenzene-Xylene Concentrate

In order to separate ethylbenzene and xylenes from the product of the smooth catalytic aromatization of
27-134° fraction, we made use of azeotropic distillation with methanol [13]. There are indications in the
ature [14] that this method is unsatisfactory when the boiling points of the azeotropic component (methanol)
of the hydrocarbons that are removed with it differ by more than 50°. This method was therefore checked on
tificial mixture of ethylbenzene and the dearomatized gasoline fraction (b.p. 134-138° after treatment with
eum). It was established in this way that methanol is quite suitable for the separation of ethylbenzene from
orresponding gasoline fraction.

In order that the separation of ethylbenzene from the aromatization product from the 127-134° fraction
be as complete as possible, we carried out the fractionation with a large excess of methanol. The opera-
was carried out in two stages. Methanol was added to the aromatization product so that the ratio of non-
atics to methanol became 1:2 or 1:3. The mixture obtained was distilled through a column of 19 theoretical
, azeotrope being separated up to 64-65°. The residue contained 70-80% of aromatic hydrocarbons. Further
nol was added to the residue to give a non-aromatic/methanol ratio of 1:7, and a second fractionation
d a residue containing aromatic hydrocarbons and methanol and practically no alkanes or cycloalkanes.
romatic hydrocarbons were readily freed from methanol by washing with water.

---

space velocity, both here and later, is expressed in liters of substance passing in one hour over one liter of
st.

As an example, we will give the results of such a distillation: Aromatization product (351 g) and methanol (328 g) were distilled through a column of 19 theoretical plates, and 435 g of azeotropic mixture was collected. Methanol (600 g) was then added to the residue, and after a second fractionation 163 g of an ethylbenzene-xylene concentrate. After being freed from methanol and dried over calcium chloride, it came over when distilled over sodium in the range 136-146°, had n_D^{20} 1.4970, d_4^{20} 0.8712, and consisted entirely of aromatic hydrocarbons.

It was established above that the aromatic hydrocarbons in the catalyzate from the 127-134° fraction consisted of 35.5% ethylbenzene and 64.5% xylenes. The concentrate that we obtained, to which we shall refer in future as the ethylbenzene-xylene concentrate, had the same composition.

Procedure Used for the Dehydrogenation of the Ethylbenzene-Xylene Concentrate, of the Ethylcyclohexane Fraction, and of the Product of the Catalytic Aromatization of the Latter at 300°

Dehydrogenation was carried out over a catalyst based on vanadium and aluminum oxides. The catalyst was contained in a silica tube, 20 mm in diameter. The tube was placed in an electric furnace, which was provided with a thermoregulator and a mercury relay. The temperature was measured by means of a thermocouple, contained in a silica jacket inserted in the layer of catalyst and connected to a potentiometer. Temperature variations were not greater than +1°. At the entrance to the reaction tube there was a three-way junction connecting the thermocouple, the automatic buret for delivery of the material to be dehydrogenated, and a Kipp's carbon dioxide generator. The rate of delivery of carbon dioxide was regulated by the aid of a flow-meter. At its exit the reaction tube was connected to a receiver, which was well cooled in ice. The content of styrene in the dehydration catalyzate was determined by titration according to Rosenmund's method [15]. In all experiments the material to be dehydrogenated was diluted with carbon dioxide, the volume ratio being kept constant (5.6 liter of CO_2 to 15 ml of liquid material).

Dehydrogenation of the Ethylbenzene-Xylene Concentrate

The principal results obtained in the dehydrogenation of the ethylbenzene-xylene concentrate are given in Table 1. For comparison, results are given of experiments on pure ethylbenzene carried out under similar conditions. The last column of the table contains values for the degree of conversion of ethylbenzene into styrene. These values are calculated from the ratio $(a \cdot 100)/b$, where a is the styrene content of the dehydrogenation catalyzate, and b is the ethylbenzene content of the material to be dehydrogenated.

The high degree of conversion of the ethylbenzene present in the ethylbenzene-xylene concentrate in comparison with that of pure ethylbenzene is noteworthy. An increase in the degree of dehydrogenation of ethylbenzene occurring when it is diluted with xylenes has been noted by other investigators. Marukyan [16] studied the dehydrogenation of ethylbenzene in admixture with xylenes at 625° over a catalyst based on copper and chromium oxides and established that reduction of the concentration of ethylbenzene in the initial mixture of 34% results in its being completely dehydrogenated.

Determination by the Polymerization Method of the Styrene Content of the Catalyzates Obtained by Dehydrogenation of the Ethylbenzene-Xylene Condensate

The combined catalyzates from a number of experiments on the dehydrogenation of the ethylbenzene-xylene concentrate was found by Rosenmund's titration method to contain 22.8% of styrene. It was considered interesting to check this result by another method. For this purpose, the catalyzate (81 g) and benzoyl peroxide (0.8 g) were sealed in a tube, which was heated at 150° for 50 hrs. The catalyzate that had been treated in this way was distilled from a Claisen flask under 150 mm pressure. The greater part of it distilled in the range 85-90° and had n_D^{20} 1.4985. The residue was then placed under vacuum, warmed gently until effervescence ceased, and allowed to cool. 19.4 g of solid yellow polymer was obtained, i.e. 22.9% of the weight of original catalyzate (after making a correction for benzoyl peroxide). Hence, the value of the styrene content of the dehydrogenation catalyzate determined by titration is almost identical with that obtained by the polymerization method.

Dehydrogenation of the 127-134° Fraction and of the Product of its Smooth Aromatization

The original fraction of b.p. 127-134° contained only 16.7% of ethylcyclohexane. An investigation of the direct dehydrogenation of ethylcyclohexane to styrene at such low concentrations could not give satisfactory results.

Nevertheless, comparison of the results of the dehydrogenation of the original fraction with those for the product of its smooth aromatization permitted an approximate appraisal of the effectiveness of prior aromatization of the fraction. Such a comparison made it possible to find out whether the first variant for the dehydrogenation of the ethylcyclohexane fraction referred to above has any advantage.

TABLE 1

Dehydrogenation of the Ethylbenzene-Xylene Concentrate at a Space Velocity of 0.3

Temp. of expt. °C	Material to be dehydrogenated	Amt. of material taken (g)	Catalyzate obtained (g)	Yield of catalyzate % on material taken	Styrene content of catalyzate %	Degree of conversion of ethylbenzene %
575	Ethylbenzene-xylene concentrate	13.1	10.5	80	19.3	68
575	Pure ethylbenzene	13.1	11.5	88	43.1	43
600	Ethylbenzene-xylene concentrate	14.8	10.8	73	20.8	74
600	Ditto	14.8	10.7	72	20.8	74
600	Pure ethylbenzene	14.9	11.7	78	50.9	51

It may be expected that dehydrogenation of ethylcyclohexane to styrene proceeds in two stages:

$$C_6H_{11}C_2H_5 \longrightarrow C_6H_5C_2H_5 + 3H_2 \longrightarrow C_6H_5CH{=}CH_2 + 4H_2.$$

The first stage of this reaction has already been realized in the smooth aromatization of the ethylcyclohexane fraction; simultaneously, dimethylcyclohexanes present in the fraction were dehydrogenated also, giving xylenes. The comparison referred to above showed, therefore, whether the performance of this reaction in two distinct stages (ethylcyclohexane being present in the fraction at low concentration) could lead to better results than direct dehydrogenation of ethylcyclohexane to styrene. The results of the dehydrogenation of the 127-134° fraction and of its aromatization product are given in Table 2. A measure of the activity of the catalyst is obtained from the results of experiments on pure ethylbenzene, which were produced under similar conditions.

The results of the experiments showed that prior aromatization of the original 127-134° fraction had no appreciable effect on the results of the subsequent dehydrogenation of this fraction. The styrene content of the catalyzates produced by dehydrogenation of the original fraction was practically identical to that of the catalyzates produced by dehydrogenation of the product of the smooth aromatization of this fraction. Hence, the first variant of the dehydrogenation of the ethylcyclohexane fraction (for low concentrations of ethylcyclohexane in the fraction) has no advantage over the third variant (see above), and performance of the reaction in two distinct stages gives results that do not differ under the conditions investigated from results obtained by the direct dehydrogenation of ethylcyclohexane to styrene. It should be noted that the results of these experiments are in agreement with the results of one of us, working with Usov and Marukyan [10].

The results that we have obtained have prompted us to investigate the dehydrogenation of pure ethylcyclohexane to styrene. The results of this work will be published later.

SUMMARY

1. A study has been made of the conditions required for the catalytic dehydrogenation with formation of styrene of the ethylcyclohexane fraction (127-134°) of Maikop straight-distillate gasoline in contact with a catalyst based on the oxides of vanadium and aluminum.

2. Results have been obtained for dehydrogenation to styrene under different conditions of the fraction mentioned, of the catalyzate obtained by the smooth dehydrogenation of the six-membered cycloalkanes (ethyl- and dimethyl-cyclohexanes) contained in the fraction in presence of platinized charcoal at 300°, and also of an ethylbenzene-xylene concentrate obtained from this catalyzate.

3. It has been shown that as a result of dehydrogenation of the ethylcyclohexane fraction, and also of the product of its catalytic aromatization at 300°, 11-14% of styrene is obtained. When the catalytic dehydrogenation is carried out on the ethylbenzene-xylene concentrate, the yields of styrene rise to 22-23%.

TABLE 2

Dehydrogenation of the 127-134° Fraction and of the Product of its Smooth Aromatization

Expt. No.	Temp. of expt. (°C)	Material to be dehydrogenated	Space velocity	Amt. of material taken, g	Catalyzate obtained (g)	Yield of catalyzate % on material taken	Styrene content of catalyzate (%)
12	547	Pure ethylbenzene	0.31	13.1	11.5	88	32.5
15	547	Product of aromatization of fraction	0.30	11.8	10.1	86	12.4
17	547	127-134° fraction	0.30	11.8	9.7	82	10.9
20	547	Ditto	0.14	11.7	8.6	73	13.5
24	575	Pure ethylbenzene	0.30	13.1	11.5	88	43.1
16	575	Product of aromatization of fraction	0.30	11.8	8.4	71	13.8
18	575	127-134° fraction	0.30	11.7	7.6	65	11.3
19	575	Ditto	0.14	15.6	8.8	56	12.2

4. It has been shown that prior aromatization of the original fraction has no appreciable effect on the results of its high-temperature dehydrogenation.

Received October 26, 1951

Institute of Organic Chemistry
of the USSR Academy of Sciences

LITERATURE CITED

[1] B. N. Dolgov. Catalysis in Organic Chemistry. State Chem. Press. Moscow, 1949; p. 195.

[2] N. V. Shorygina. Styrene – Its Polymers and Copolymers. State Chem. Press. Moscow, 1949; p.12.

[3] N. D. Zelinsky, G. M. Marukyan, and O. K. Bogdanova. J. Appl. Chem., 14, 161 (1941).

[4] N. D. Zelinsky and N. I. Shuykin. J. Gen. Chem., 4, 901 (1934).

[5] N. D. Zelinsky and N. I. Shuykin. Bull. OMEN Acad. Sci. USSR, No. 2, 229 (1935).

[6] N. D. Zelinsky and N. I. Shuykin. J. Appl. Chem., 9, 260 (1936).

[7] S. S. Nametkin. Chemistry of Petroleum. United State Sci. Tech. Press. Moscow. 1939; p.219.

[8] N. I. Shuykin. Prog. Chem., 15, 343 (1946).

[9] A. F. Plate. Catalytic Aromatization of Paraffin Hydrocarbons. Acad. Sci. USSR Press. Moscow and Leningrad, 1948; p. 134.

[10] N. I. Shuykin, Yu. N. Usov, and G. M. Marukyan. Sci. Mem. Moscow State Univ. Organic Chem., Book VIII, issue 151, p. 191 (1951).

[11] B. L. Moldavsky, G. D. Kamusher, and M. V. Kobylskaya. J. Gen. Chem., 7, 167 (1937).

[12] G. N. Maslyansky and T. S. Berlin. J. Gen. Chem. 16, 1643 (1946).

[13] B. B. Kaminer, L. A. Fomenko, and A. S. Velikovsky. Trans. ' Central Sci. Res. Inst Aviation Fuel and Oils. Aromatization of Hydrocarbons derived from Petroleum 4, 37 (1947).

[14] A. N. Sachanen, The chemical constituents of petroleum, N.Y. 1945, p. 60.

[15] K. W. Rosenmund and W. Kuhnhenn, Z. f. Untersuch. d. Nahrungs und Genussmittel 46, 154 (1923).

[16] G. M. Marukyan. J. Appl. Chem. 19, 1277 (1946).

BLANK
PAGE

HEXADECYL ESTERS OF CERTAIN INORGANIC ACIDS

B. A. Arbuzov and V. S. Vinogradova

In the course of work on the structures of esters of inorganic acids, which we studied by the aid of parachor [1] and viscosity measurements, we found it necessary to synthesize esters containing long hydrocarbon radicals. We have recently synthesized a number of esters, including the hexadecyl esters of phosphorous, silicic, and boric acids. We found that these esters, in spite of their high molecular weights, could be distilled in a high vacuum.

We prepared trihexadecyl phosphite by transesterification of triethyl phosphite with 1-hexadecanol in presence of a small amount of phosphoric acid. It is a colorless liquid, non-wetting to glass; it has b.p. 288-290°/4 mm, and it crystallizes at room temperature to a white mass, m.p. 46-47°. After recrystallization from hexane under cooling, trihexadecyl phosphite has m.p. 51°.

Davey [2] has recently prepared trihexadecyl phosphite by the action of phosphorus trichloride in hexadecanol in presence of pyridine. Davey gives the m.p. as 67° and does not indicate the b.p. We have subjected the substance to repeated recrystallization, but have been unable to obtain a melting point of 67°. Tetrahexadecyl orthosilicate was prepared by Helferich and Hausen [3] as a solid of m.p. 46.5-49.5°. Attempts to distil it under reduced pressure failed.

We have prepared tetrahexadecyl orthosilicate by the transesterification of the tetraethyl ester with hexadecanol. The tetrahexadecyl ester distils in a high vacuum without any signs of decomposition; it is a colorless transparent liquid, rapidly crystallizing on cooling: b.p. 353-355°/0.0117 mm or 363-366°/0.2 mm; m.p. 44.5-45°. It should be mentioned that tetrahexadecyl orthosilicate contains 64 carbon atoms and has a molecular weight of about 1000 (995.0).

Trihexadecyl borate was obtained by the esterification of boric acid with hexadecanol. It is a colorless liquid, non-wetting to glass, b.p. 328-329°/< 0.5 mm; rapidly crystallizes at room temperature, m.p. 43-44°.

EXPERIMENTAL

Distillation of the esters was carried out from a Claisen-type flask containing glass wool and having a long exit tube fused on in a low position; the receivers were fused on to this tube, and the selection of fractions was made by rotating the whole apparatus. When distillation was complete, the receivers were fused off.

Trihexadecyl Phosphite. Triethyl phosphite (3.6 g) and 1-hexadecanol (14 g) were introduced into the distillation flask, and sirupy phosphoric acid (2 drops) was added. On heating, alcohol (2.2 g) was driven off. In the course of distillation a small amount of hexadecanol passed over, and this was followed by a colorless liquid, b.p. 288-290°/4 mm. Redistillation yielded hexadecanol and a small amount of the phosphite, m.p. 46-47°. Recrystallization from hexane, with cooling to 0°, yielded a product of m.p. 51°.

Found %: P 4.44

$C_{48}H_{99}O_3P$. Calculated %: P 4.10

Tetrahexadecyl Orthosilicate. 30 g of hexadecanol and 5.8 g of the ethyl ester were taken. No ethanol came over on heating. Phosphoric acid (2 drops) was added. Alcohol (4.2 g) came over. The final temperature of the bath was 220°. When the mixture was distilled, a small amount of hexadecanol was driven off, and then, at 362-365°/0.1 mm, a colorless transparent liquid came over; it rapidly crystallized on cooling. After repeated distillation: b.p. 353-355°/0.0117 mm, 363-366°/0.2 mm; m.p. 44.5-45°.

Trihexadecyl Borate. 1-Hexadecanol (10 g) and boric acid (0.85 g) were placed in a flask and heated. Water came off (bath temperature up to 200°) and was removed towards the end of the reaction under suction from a water pump. In the course of distillation under high vacuum, first a little hexadecanol came over, and there followed a colorless liquid, b.p. 328-331°/< 0.5 mm, which did not wet glass; it crystallized in the receiver to give a white waxlike mass. After repeated distillation; b.p. 328-329°/< 0.5 mm, m.p. 43-44°; yield 80%.

Found %: B 1.38

$C_{48}H_{99}O_3$ Calculated %: B 1.46

SUMMARY

Trihexadecyl phosphite and tetrahexadecylorthosilicate have been prepared by transesterification of the ethyl esters of the corresponding acids by means of 1-hexadecanol. Trihexadecyl borate has been prepared by the action of 1-hexadecanol on boric acid. All the esters obtained may be distilled in a high vacuum without decomposition.

Received January 5, 1952

A. M. Butlerov Chemical Research Institute
attached to the V. I. Ulyanov-Lenin Kazan
State University

LITERATURE CITED

[1] V. S. Vinogradova. Sci. Memoirs Kazan State Univ., 110, Book 9, 1 (1950).

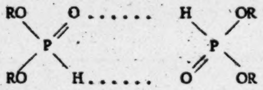
[2] W. Davey, Ind. Eng. Chem. 42, 1841 (1950).

[3] B. Helferich and J. Hausen, Ber. 57, 795 (1924).

VISCOSITY AND STRUCTURE OF DIALKYLPHOSPHOROUS ACIDS[**]

B. A. Arbuzov and V. S. Vinogradova

On the basis of studies of Raman spectra, A. E. Arbuzov, Batuev, and Vinogradova [1] concluded that the lower dialkylphosphorous acids are associated, forming dimers by the aid of hydrogen bonds



We came to similar conclusions for the lower members of the series from a study of their parachors [2] and from direct molecular weight determinations in benzene solution [3]. Dimethylphosphorous acid is found in the monomeric condition only in very dilute solution.

TABLE 1

Name of acid	Solvent	Concentration%	η_{sp}^{20} (1.4%)·10^{-3}	η_{sp} (1.4%)·10^{-4} calculated		$Z_\eta \cdot 10^{-4}$ found	$Z_\eta \cdot 10^{-4}$ calculated	
				monomer	dimer		monomer	dimer
Dibutylphosphorous	CCl_4	2.82 3.83 5.35	11.3 13.6 12.8	16.5	21.0	8.1 9.7 9.1	11.9	15.1
Dihexylphosphorous	CCl_4	2.68 3.70 4.01	24.0 22.4 20.0	22.5	27.0	17.2 16.1 14.2	16.2	19.4
Dicyclohexylphosphorous[*]	C_6H_6	3.66 5.51	16.3 18.0	19.5	23.4	11.6 12.8	14.0	16.7
Dioctylphosphorous	CCl_6	2.62 3.15 5.07	22.5 23.9 24.1	28.5	33.0	16.1 17.2 17.2	20.5	23.8
Dinonylphosphorous	CCl_4	2.68 3.48	31.5 26.7	31.5	36.0	22.5 13.0	22.7	25.9
Didecylphosphorous	CCl_4	2.91 3.18	30.2 33.1	34.5	39.0	21.6 23.7	25.0	28.1
Dihexadecylphosphorous	CCl_4	2.70 2.44	55.2 56.5	52.5	58.5	39.4 40.3	37.8	42.1

The higher members of the dialkylphosphorous acid series (dihexyl-, diheptyl-, dioctyl-phosphorous acids) are monomeric both in solution, and in the liquid state. Kosalapoff [4] has found by molecular weight determinations in dilute benzene and naphthalene solutions that diethyl- and dibutyl-phosphorous acids are monomeric. The infrared spectra of the lower dialkylphosphorous acids point to their association [5]. Staudinger [6] showed that measurements of the viscosity of the higher fatty acids in dilute solution indicate that they are associated into dimers.

In the present communication we give our results on the measurement of the viscosities of solutions of dialkylphosphorous acids containing fairly long hydrocarbon radicals (Table 1).

---

[*] For calculation of the theoretical value of the viscosity, a six-membered ring is taken as six members.

[**] The original terminology is retained, dialkylphosphorous acid being a non-committal term for what may be a dialkyl phosphonate, a dialkyl hydrogen phosphite, or a tautomeric mixture of these. - Publisher.

TABLE 2

Name of acid	Solvent	Concentration%	$\eta^{20}_{equiv} \cdot 10^{-3}$ of monomer		$\eta^{20}_{equiv} \cdot 10^{-3}$ of dimer	
			found	calculated	found	calculated
			η (1.76%)		η(2.06%)	
Dibutylphosphorous	CCl_4	2.82	14.3	21.0	16.6	31.2
		3.83	17.2		20.0	
		5.35	16.1		18.8	
			η(1.67%)		η(2.78%)	
Dihexylphosphorous	CCl_4	2.68	28.7	27.0	47.8	54.1
		3.70	26.8		44.7	
		4.10	23.8		39.6	
			η(1.64%)		η(2.73%)	
Dicyclohexylphosphorous	C_6H_6	3.66	19.1	22.9	31.8	45.8
		5.51	21.1		35.1	
			η(1.61%)		η(2.21%)	
Dioctylphosphorous	CCl_4	2.62	26.0	33.1	35.1	66.2
		3.15	27.6		38.0	
		5.07	27.7		38.1	
			η(1.59%)		η(2.78%)	
Dinonylphosphorous	CCl_4	2.68	35.8	36.1	62.7	72.2
		3.48	30.3		53.1	
			η(1.57%)		η(2.79%)	
Didecylphosphorous	CCl_4	2.91	34.1	39.1	60.4	78.3
		3.18	37.3		66.0	
			η(1.51%)		η(2.72%)	
Dihexadecylphosphorous	CCl_4	2.70	59.6	57.3	107.4	114.6
		2.44	60.9		109.8	

As the results in Table 1 show, the values of η_{sp} (1.4%) and Z_η, calculated for the monomeric and for the dimeric forms of the dialkylphosphorous acid, do not differ greatly, but the experimentally found values correspond more closely to the monomeric forms.

A clearer picture is obtained for the values of η_{equiv}, which takes into account not only the length of the longest chain in the molecule, but also the weight of the whole molecule in its relation to the members of the longest chain [7]. The results obtained are given in Table 2.

The results in Table 2 show that, according to viscosity measurements, the dialkylphosphorous acids occur in the monomeric form.

EXPERIMENTAL

The dialkyphosphorous acids were prepared by the action of phosphorous trichloride on the corresponding alcohols, or by the transesterification of diethylphosphorous acid. The following acids were prepared by the action of phosphorous trichloride on the corresponding alcohols:

1. Dibutylphosphorous acid: b.p. 115° at 10 mm; n_D^{20} 1.4240; d_0^{20} 0.9888 [8].
2. Dihexylphosphorous acid: b.p. 145-146° at 2 mm; n_D^{20} 1.4335; d_0^{20} 0.9486 [8].
3. Dioctylphosphorous acid: b.p. 185-187° at 2 mm; n_D^{20} 1.4422; d_0^{20} 0.9286 [8].

4. Dicyclohexylphosphorous acid: b.p. 155-155.2° at 2 mm; n_D^{20} 1.4778; d_0^{20} 1.0815 [9].

Dihexyl- and dioctyl-phosphorous acids were obtained also by the transesterification reaction. Dinonyl-, didecyl-, dihexadecyl-, bis(β-phenylethyl)-, (ethyl)hexyl-, and (ethyl)octyl-phosphorous acids were obtained for the first time.

Viscosity results for (ethyl)-hexylphosphorous acid are not given, for the chain is not sufficiently long for viscosimetric determinations. The viscosities of (ethyl)octyl- and bis(β-phenylethyl)-phosphorous acids were not determined.

Transesterification of diethylphosphorous acid by the higher alcohols was carried out in presence of 1-2 drops of concentrated phosphoric acid. When ethanol had ceased to come over, the residue was vacuum-distilled. In the distillation there were obtained appreciable intermediate fractions that gave, on being repeatedly distilled, an appreciable amount of dialkylphosphorous acids containing higher radicals. It is very probable that in the course of the fractionations there is a redistribution of the radicals of the mixed esters of phosphorous acid that have been formed.

Transesterification of Diethylphosphorous Acid by Hexyl Alcohol

The amounts taken were: diethylphosphorous acid 7 g, hexyl alcohol 14 g (theoretical: 10 g). Ethanol began to come over at a bath temperature of 140-150°; 5.5 ml came over. 5.5 g of hexyl alcohol and intermediate fractions came over and 10 g of the fraction b.p. 142-150°/4 mm. A second distillation gave dihexylphosphorous acid (6 g): b.p. 138.5-139° at 2 mm; n_D^{20} 1.4332.

Transesterification of Diethylphosphorous Acid by Octyl Alcohol

Carried out by a similar method. B.p. 191-192° at 4.5 mm; d_0^{20} 0.9263; n_D^{20} 1.4410.

Transesterification by Nonyl Alcohol

The amounts taken were: diethylphosphorous acid 7 g, nonyl alcohol 15 g. Alcohol began to come over at a bath temperature of 150°. 4.5 ml of alcohol was driven off. On fractionation there was obtained 9 g of a fraction b.p. 199-206° at 4 mm. On redistillation there was obtained dinonylphosphorous acid, b.p. 211-212° at 5 mm; 174.5-175.5° at 0.04 mm; n_D^{20} 1.4458; d_0^{20} 0.9212.

Found %: P 9.38; 9.58

$C_{18}H_{39}O_3P$. Calculated %: P 9.26

Transesterification by Decyl Alcohol

The amounts taken were: diethylphosphorous acid 5 g, decyl alcohol 13 g. 3.5 ml of ethanol was driven off. Fractionation yielded 8 g of fraction, b.p. 187-194° at 0.03 mm. Refractionation gave didecylphosphorous acid, b.p. 190-191° at 0.04 mm; n_D^{19} 1.4502; d_0^{20} 0.9157.

Found %: P 8.63; 8.55

$C_{20}H_{43}O_3P$. Calculated %: P 8.54

Transesterification by β-Phenylethanol

The amounts taken were: diethylphosphorous acid 10 g, β-phenylethanol 23 g (theoretical: 17.5 g). 8 ml of alcohol was driven off. On distillation in high vacuum, the following fractions were obtained:

Fraction 1, b.p. to 173° at 0.05 mm
Fraction 2, b.p. 173-209° at 0.05-0.1 mm – 9.5 g.

Decomposition set in. A large residue remained in the flask as a transparent viscous mass. Fraction 2 has a beautiful violet fluorescence. On redistillation it gave a fraction, b.p. 183.5-185.5° at 0.05 mm; n_D^{21} 1.5465; d_0^{20} 1.1333. The substance has a beautiful violet fluorescence.

Found %: P 10.25

$C_{16}H_{19}O_3P$. Calculated %: P 10.69

Transesterification by Hexadecyl Alcohol

The amounts taken were: diethylphosphorous acid 5 g, hexadecyl alcohol 18 g. Alcohol began to come over at a bath temperature of 170°. Towards the end the bath temperature was raised to 220°. On distillation the following fractions were obtained:

Fraction 1, b.p. 115-130° at 0.07 mm – 11 g
Fraction 2, b.p. 130-230° at 0.1 mm

At this point decomposition set in, and low-boiling fractions came over. On refractionation of fraction 2, decomposition again set in with formation of readily volatile products. Fractionation of fractions 1 and 2 over sodium gave a product that corresponded, according to its constants, to 1-hexadecene: b.p. 126-129° at 3 mm; n_D^{17} 1.4462, d_0^{20} 0.7870.

Duplicate experiment. The amounts taken were: diethylphosphorous acid 4.5 g and hexadecyl alcohol 15 g. Alcohol began to come over at 150°, and 2 ml was collected. Volatile products were driven off in a high vacuum in an apparatus having fused-on receivers. When the temperature on the thermometer was 200° and the pressure was 0.015 mm, boiling commenced, but slight decomposition occurred at the same time and distillation was stopped. A transparent, colorless liquid remained in the flask; on standing, it crystallized (11 g, m.p. 44-45°). M.p. after recrystallization from hexane: 51-52°. M.p. in admixture with hexadecyl alcohol: 51-52°. However, analysis showed that the substance was dihexadecylphosphorous acid.

Found %: P 5.84
$C_{32}H_{67}O_3P$. Calculated %: P 5.84

Preparation of (Ethyl)-hexylphosphorous Acid

The amounts taken were: diethylphosphorous acid 14 g, hexyl alcohol 10 g. Alcohol began to come over at a bath temperature of 170°; 5.5 ml of alcohol was collected. Fractionation gave the following fractions:

Fraction 1, b.p. to 95° at 2 mm
Fraction 2, b.p. 96-106° at 2 mm
Fraction 3, b.p. 106-149° at 2 mm

After repeated fractionation, a fraction (6 g) having the following constants was isolated: b.p. 104-105° at 3.5 mm; n_D^{20} 1.4268; d_0^{20} 0.9883.

Found %: P 16.09; 15.94
$C_8H_{19}O_3P$. Calculated %: P 15.97

From the higher fractions dihexylphosphorous acid was obtained: b.p. 138-141° at 3.5 mm; n_D^{20} 1.4332.

Preparation of (Ethyl)-octylphosphorous Acid

The amounts taken were: diethylphosphorous acid 15 g, octyl alcohol 14 g. 6 ml of alcohol was distilled off. Fractionation yielded the following fractions:

Fraction 1, b.p. 64-129° at 6mm – 6 g
Fraction 2, b.p. 129-155° at 7 mm – 7 g
Fraction 3, b.p. 155-200° at 7 mm – 10 g

After further fractionation there were isolated: diethylphosphorous acid, b.p. 61-62° at 7 mm; dioctylphosphorous acid, b.p. 191-194° at 6.5 mm; and (ethyl)-octylphosphorous acid, b.p. 126-128.5° at 4.5 mm; n_D^{20} 1.4312; d_0^{20} 0.9779.

Found %: P 14.22
$C_{10}H_{23}O_3P$. Calculated %: P 13.89

During each distillation, a readily volatile fraction (diethylphosphorous acid) and a fraction corresponding to dioctylphosphorous acid were separated.

SUMMARY

1. Viscosity determinations on dialkylphosphorous acids in dilute carbon tetrachloride or benzene solution give values of η_{equiv} that indicate that these substances are in the monomeric condition.

2. By transesterification of diethylphosphorous acid by the appropriate alcohol the following substances have been synthesized for the first time: dinonyl-, didecyl-, dihexadecyl-, bis(β-phenylethyl)-, (ethyl)hexyl-, and (ethyl)octyl-phosphorous acids.

Received January 5, 1952

A. M. Butlerov Chemical Research Institute attached to
the V. I. Ulyanov-Lenin Kazan State University

LITERATURE CITED

[1] A. E. Arbuzov, M. I. Batuev, and V. S. Vinogradova. Rep. Acad. Sci. USSR, 54, 60[illegible] (1946).

[2] B. A. Arbuzov, V. S. Vinogradova. Bull. Acad. Sci. USSR. Div. Chem. Sci., 617 (1947).

[3] B. A. Arbuzov and V. S. Vinogradova. Rep. Acad. Sci. USSR, 72, 695 (1950).

[4] G. Kosolapoff, J. Chem. Soc. 3536 (1950).

[5] Meyzick and Thomson, J. Chem. Soc. 225 (1950).

[6] H. Staudinger and E. Ochiai, Z. phys. Chem. 158, 45 (1932).

[7] H. Staudinger. Macromolecular Organic Compounds. United Sci. Tech. Press. 1935, p. 65.

[8] V. S. Vinogradova. Sci. Mem. Kazan State. Univ. 110, Book 9, 69 (1950).

[9] H. G. Cook, I. D. Ilett, B. C. Saunders, G. I. Steacly, H. G. Watson, I. G. E. Wilding and S. J. Woodcock, J. Chem. Soc. 2926 (1949).

BLANK
PAGE

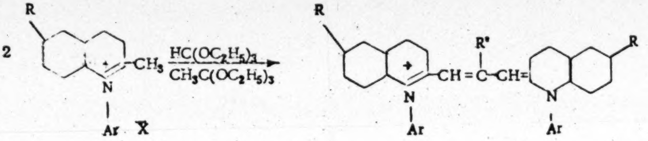
CYANINE DYES

COMMUNICATION 1. SYMMETRICAL N-ARYLQUINOCYANINES

G. T. Pilyugin

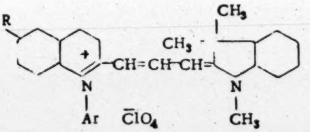
As we have already shown [1], when secondary aromatic amines react with paraldehyde, cyclization occurs with formation of a pyridine ring, and quinaldine derivatives having an aryl radical on the hetero nitrogen atom are obtained. Having thus prepared such aryl-substituted quinaldine derivatives for the first time, we succeeded in converting them, concurrently with cyclization, into the corresponding quaternary salts, which, owing to the presence of a reactive methyl group in the α-position, are susceptible to many chemical changes. As a result we have the prospect of preparing new organic compounds of various classes having the most varied properties. Our quaternary quinolinium salts with aryl radicals on the hetero N have been subjected to the cyanine condensation, yielding carbocyanines of symmetrical and of unsymmetrical structure.

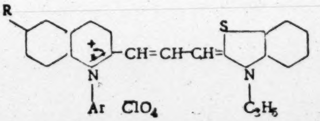
Thus, by condensation of a N-arylquinolinium salt with orthoformic or orthoacetic ester, symmetrical dyes are obtained according to the scheme [2]:



where Ar = C_6H_5; $C_6H_4CH_3(o,p)$; $C_{10}H_7(\alpha,\beta)$; R = CH_3, R' = H, CH_3; X = I, ClO_4.

When the quaternary salts react with 1,3,3-trimethyl-2-(2-N-phenylacetamidovinyl)-3H-pseudoindolium iodide or with 3-ethyl-2-(2-N-phenylacetamidovinyl)-benzothiazolium iodide, unsymmetrical carbocyanines are obtained [3]:





In this paper we shall examine the symmetrical carbocyanines that we have prepared. They are given in the following table.

It must be pointed out that the aryl radical on the hetero N considerably activates the α-methyl group; this is confirmed by the readiness with which the trinuclear quaternary salts undergo the cyanine condensation, even in the form of halides (but not arylsulfonates), which do not give the cyanine condensation at all when there is an alkyl on the hetero N. Also, the high reactivity is confirmed by the fact that the quinocyanine condensation occurs with orthoacetic ester; this is not so when there is an alkyl radical on the hetero N. This increased reactivity may be explained by the change resulting in the mutual electronic effects between the α-methyl and the radical on the hetero N when the latter is changed from alkyl to aryl.

It can be seen from the absorption spectra obtained that the introduction of methyl or of a fused benzene ring in various positions in the dye molecule leads to various bathochromic shifts in the absorption maximum, the effect being relatively great when the groups are introduced at some point in the benzene ring of the molecule, and considerably less when they are introduced into the grouping attached to the hetero nitrogen. Thus, the methyl group introduced symmetrically in the 6,6'-positions displaces the absorption maximum of the dye towards

TABLE

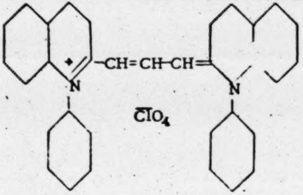
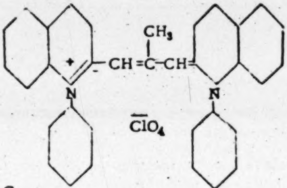
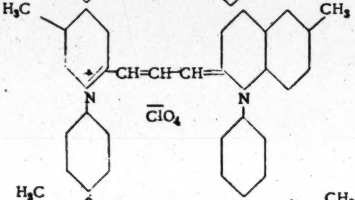
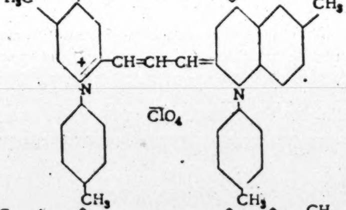
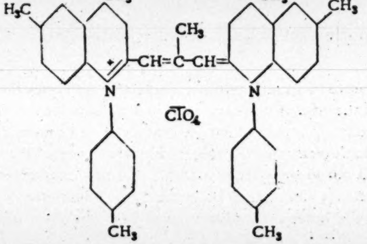
No.	Formula of dye	Absorption maximum (mμ)
1		614
2		610
3		620
4		622
5		618

TABLE (Continued)

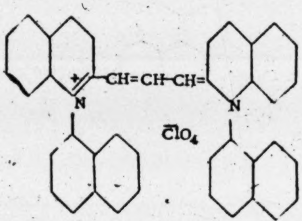
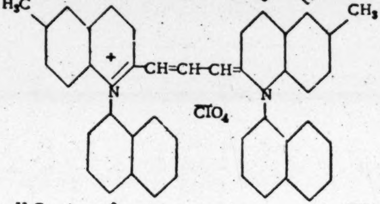
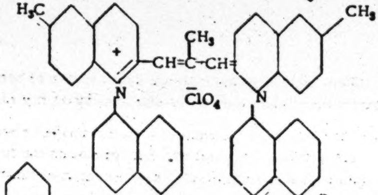
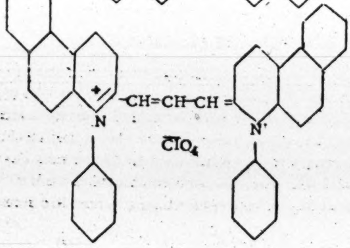
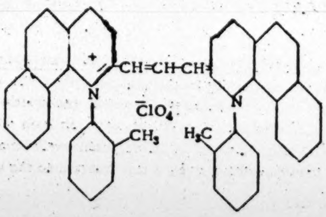
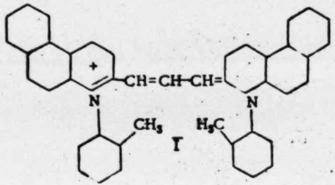
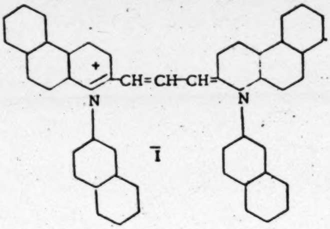
No.	Formula of dye	Absorption maximum (mμ)
6	 + CH=CH–CH= N N $\bar{C}lO_4$	618
7	 H_3C CH_3 + CH=CH–CH= N N $\bar{C}lO_4$	625
8	 H_3C CH_3 CH_3 + CH=C–CH= N N $\bar{C}lO_4$	620
9	 + CH=CH–CH = N N $\bar{C}lO_4$	645
10	 + CH=CH–CH= N N $\bar{C}lO_4$ CH_3 H_3C	642

TABLE (Continued)

No.	Formula of dye	Absorption maximum (mμ)
11		644
12		654

the red end of the spectrum by 6 mμ (compared with the unsubstituted dye). Fusion of benzene rings at the 5,6- and 5',6'-positions in the symmetrical dye displaces the absorption maximum by 31 mμ (dyes 1 and 9).

When similar substituents are introduced into the radical attached to the hetero nitrogen, the bathochromic shifts in the absorption maximum are considerably smaller. Aryl groups on the hetero nitrogen, when compared with alkyl groups, are found to cause a bathochromic displacement in the absorption maximum of the cyanine dye molecule.

EXPERIMENTAL

1. Bis-2-(1-phenylquinoline)-trimethinecyanine perchlorate. 1-Phenylquinaldinium perchlorate (1 g) and ethyl orthoformate (1 g) were condensed in pyridine (1.5 g), the mixture being boiled gently under reflux for 20 min. The dye was formed very readily: as soon as heating was commenced, the reaction mixture took on an intense blue color. The dye was isolated by adding alcohol (4 ml) to the pyridine solution, heating to the boil, and diluting with hot water (4 ml). On the next day the precipitated dye was filtered off and then washed with water and with small amounts of alcohol and ether. The dye, purified by recrystallization from alcohol, consisted of beautiful green crystals having a metallic luster, m.p. 276° (decomp.), absorption max. 614 mμ (0.2 g, 25%).

Found %: Cl 6.21

$C_{33}H_{25}N_2O_4Cl$. Calculated %: Cl 6.46

2. [Bis-2-(1-phenylquinoline)]-β-methyltrimethinecyanine perchlorate. 1-Phenylquinaldine perchlorate (1.5 g) was dissolved in pyridine (3 ml), and orthoacetic ester (3 g) was added. The mixture was boiled gently for 3 hrs. It was then cooled, and the dye was precipitated by means of ether, filtered off, and washed with ether and alcohol. The dye, after recrystallization from alcohol, was a dark-blue powder having a metallic luster, m.p. 231° (decomp.) (0.46 g, 18%). The absorption maximum of the dye in ethanol solution is at 610 mμ, i.e. displaced hypsochromically by 4 mμ relative to the unsubstituted dye.

Found %: Cl 6.11

$C_{34}H_{27}N_2O_4Cl$. Calculated %: Cl 6.30

3. Bis-2-(6-methyl-1-phenylquinoline)trimethinecyanine perchlorate. 2,6-Dimethyl-1-phenylquinolinium perchlorate (0.3 g), orthoformic ester (1 ml), and pyridine (1.5 g) were boiled together in a flask under reflux for 50 min. The mixture was cooled, and the dye formed was precipitated by ether and dissolved in a small amount of alcohol. On the next day the dye was filtered off and washed with alcohol and ether. The dye, after recrystallization from alcohol, was a finely crystalline dark-blue powder, m.p. 270° (0.1 g, 38.4%). Absorption maximum 620 mμ.

Found %: Cl 5.90
$C_{35}H_{29}N_2O_4Cl$. Calculated %: Cl 6.15

4. Bis-2-(6-methyl-1-p-tolylquinoline)trimethinecyanine perchlorate. 2,6-Dimethyl-1-p-tolylquinolinium perchlorate (0.5 g) was dissolved in pyridine (3 ml), ethyl orthoformate (0.25 g) was added, and the mixture was heated at the boil for 1 hr. As heating proceeded, the reaction mixture acquired an intense blue color. On the next day the precipitated crystals were filtered off and washed with alcohol and ether. The dye was obtained, after recrystallization, in the form of dark-green crystals having a metallic luster, m.p. 302° (0.16 g, 36.3%). Absorption maximum 622 mμ.

Found %: Cl 5.98
$C_{37}H_{33}N_2O_4Cl$. Calculated %: Cl 5.87

5. [Bis-2-(6-methyl-1-p-tolylquinoline)]-β-methyltrimethinecyanine perchlorate. The quaternary salt (0.4 g) was dissolved in pyridine (3 ml), and orthoacetic ester (0.25 g) was added. The mixture was boiled for 2 hrs and became progressively more intense in color. The dye was precipitated with ether, filtered off, dissolved in a small amount of alcohol, and precipitated with a saturated solution of potassium chlorate, the solutions of dye and of perchlorate being first brought to the boil. A small amount of water was added and the solution was boiled. When the solution was cooled, the dye precipitated and was then filtered off and washed with ether. It was recrystallized from aqueous alcohol. The dye contained (0.1 g, 30%)' melted at 210° (decomp.). Absorption maximum 618 mμ, i.e. displaced relative to that of the unsubstituted dye by 4 mμ towards the short waves.

Found %: Cl 5.28
$C_{38}H_{35}N_2O_4Cl$. Calculated %: Cl 5.74

6. Bis-2-(1-(1-naphthyl)quinoline)trimethinecyanine perchlorate. 1-(1-Naphthyl)quinaldinium perchlorate (0.2 g), orthoformic ester (1 ml), and pyridine (2 ml) were boiled together for 40 min. The mixture was cooled, and the dye that had formed was precipitated by addition of ether (5 ml); it was dissolved in alcohol (2 ml) and left until the next day, when it was filtered off and washed with water, alcohol, and ether. The dye, after recrystallization from aqueous alcohol, was in the form of a finely crystalline dark-blue powder having a metallic luster, m.p. 235° (0.09 g, 25.4%). Absorption maximum 618 mμ.

Found %: Cl 5.28
$C_{41}H_{29}N_2O_4Cl$. Calculated %: Cl 5.47

7. Bis-2-(6-methyl-1-(1-naphthyl)quinoline)trimethinecyanine perchlorate.

The quaternary salt (0.4 g), orthoformic ester (0.2 ml), and pyridine (3 ml) were placed in a flask and boiled for 50 min. The contents of the flask gradually acquired a blue color. The dye was precipitated with ether, dissolved in a small amount of alcohol, and then precipitated by means of a saturated solution of potassium perchlorate. The dye, after recrystallization from aqueous alcohol, melted at 238° (decomp.) (0.15 g, 46%). Absorption maximum 625 mμ.

Found %: Cl 5.08
$C_{43}H_{33}N_2O_4Cl$. Calculated %: Cl 5.24

8. [Bis-2-(6-methyl-1-(1-naphthyl)quinoline)]-β-methyltrimethinecyanine perchlorate. The quaternary salt (0.25 g), orthoacetic ester (0.15 g), and pyridine (2 ml) were introduced into a 25 ml flask fitted with a reflux condenser. The mixture was gently boiled and given moderate shaking for 1 hr. A further amount (0.5 ml) of orthoacetic ester was then added to the reaction mixture, and heating was continued for a further 50 min. The contents were cooled, treated with ether, and dissolved in a small amount of alcohol. A saturated solution of potassium perchlorate (2 ml) was added to the hot alcoholic solution. The precipitated finely crystalline blue dye was filtered off and washed with ether and alcohol. The dye, after recrystallization from aqueous alcohol melted at 210° (decomp.) (0.1 g, 48%). Absorption maximum 620 mμ.

Found %: Cl 4.87
$C_{44}H_{35}N_2O_4Cl$. Calculated %: Cl 5.14

9. Bis-3-(4-phenylbenzo/f/quinoline)trimethinecyanine perchlorate. 3-Methyl-4-phenylbenzo/f/quinolinium perchlorate (0.2 g), orthoformic ester (0.1 g), and pyridine (3 ml) were boiled together for 40 min with continuous shaking. As heating proceeded, the reaction mixture acquired a green color. When the mixture was cooled, beautiful dark-green crystals of the dye were precipitated. They were recrystallized from aqueous alcohol (0.06 g, 41%). The m.p. of the dye was 267° (decomp). Absorption maximum 645 mμ.

Found %: Cl 5.31
$C_{41}H_{29}N_2O_4Cl$. Calculated %: Cl5.47

10. Bis-2-(1-o-tolylbenzo/h/quinoline)trimethinecyanine perchlorate. 2-Methyl-1-o-tolylbenzo/h/quinolinium perchlorate (0.2 g), orthoformic ester (0.1 g), and pyridine (3 ml) were boiled together for 1 hr. A green color developed and became more and more intense as heating continued. The solution was cooled, and the dye was precipitated with ether, filtered off, dissolved in a small amount of alcohol, and left to stand until the next day. The precipitated dye was filtered off and washed with water, alcohol, and ether. The dye, after recrystaliization from aqueous alcohol melted at 287° (decomp.) (0.08 g, 37%). Absorption maximum 642 mμ.

Found %: Cl 5.08
$C_{43}H_{33}N_2O_4Cl$. Calculated %: Cl 5.24

11. Bis-3-(4-o-tolylbenzo/f/quinoline)trimethinecyanine iodide. 3-Methyl-4-o-tolylbenzo/f/quinolinium iodide (0.2 g), orthoformic ester (1 ml), and pyridine (1 ml) were boiled and shaken continuously for 30 min. When heating was applied, the mixture at first darkened; it then took on a greenish tinge, and by the end of the heating period it had acquired an intense green color. The dye was precipitated with ether and dissolved in a small amount of alcohol. On the next day the precipitated dye was filtered off and washed with alcohol and ether. The dye, after recrystallization from aqueous alcohol, melted at 287° (decomp. (0.038 g, 22%). Absorption maximum 644 mμ.

Found %: I 17.88
$C_{43}H_{33}N_2I$. Calculated %: I 18.03

12. Bis-3-(4-(2-naphthyl)benzo/f/quinoline)trimethinecyanine iodide. 3-Methyl-4-(2-naphthyl)benzo/f/quinolinium iodide (0.4 g), pyridine (2 ml), and orthoformic ester (0.2 g) were boiled gently together for 20 min. As heating proceeded the reaction mixture gradually acquired a bright green color. The mixture was cooled, and the dye was precipitated by addition of ether. The dye powder was filtered off, washed with alcohol and ether, and recrystallized from aqueous alcohol. The dark-green dye melted, after recrystallization, at 275-278° (21% yield). Absorption maximum 654 mμ.

Found %: I 16.18
$C_{49}H_{33}N_2I$. Calculated %: I 16.36

I express my sincere thanks to V. N. Tolmachev, senior scientific worker in the Institute of Chemistry of the Kharkov State University, for help in the determination of absorption spectra.

SUMMARY

1. Starting from N-arylquinolinium salts, twelve new symmetrical carbocyanines having phenyl and naphthyl radicals on the hetero nitrogen have been prepared.

2. It has been shown that the introduction of phenyl and naphthyl radicals on the hetero nitrogen of quinocarbocyanines causes a bathochromic shift in the absorption maximum, as compared with the N-ethyl compounds, of 10-12 and 14-18 mμ respectively.

3. Introduction of a methyl group in the meso-position of the polymethine chromophore of N-aryl-carbocyanines causes an insignificant hypsochromic shift of the absorption maximum, as compared with the unsubstituted compounds.

4. The presence of aryl radicals on the hetero nitrogen of quinolinium salt increases the activity of the 2-methyl group. This is confirmed by the readiness with which complex quaternary halides undergo cyanine condensations.

Received December 1, 1951

Institute of Organic Chemistry of the
USSR Academy of Sciences
Chernovitsy State University

LITERATURE CITED

[1] G. T. Pilyugin. Bull. Acad. Sci. USSR. Div. Chem. Sci., No. 2, 353 (1952)[*]; G. T. Pilyugin and Z. Ya. Krayner. Proc. Acad. Sci. USSR, 81, 4, 609 (1951).

[2] W. Konig, Ber. 55, 3292 (1922); F. M. Hamer, J. Chem. Soc. 2796 (1927).

[3] T. Ogata, C. 1932, II, 711; Brit. pat. 34409 (ICI) C. 1931, I, 3297; H. A. Piggot, E. H. Rodd, U.S. Pat. 2071898.

---

[*] See Consultants Bureau translation, p. 347.

BLANK
PAGE

CYANINE DYES

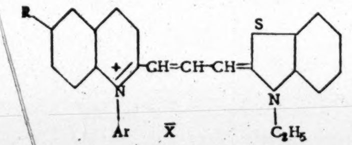
COMMUNICATION 2. UNSYMMETRICAL CARBOCYANINES FROM DERIVATIVES OF N-ARYLQUINALDINE AND OF BENZOTHIAZOLE

G. T. Pilyugin

Symmetrical quinocyanines were among the first of the cyanine dyes [1]. Also, they were among the first of the cyanine group to be examined for sensitization purposes. However, as this question developed they became displaced by thiacyanines [2], which were found to be more powerful as sensitizers than quinoline derivatives.

At the present time, among all the classes of sensitizing dyes, it is the thiacyanine class that receives the most study and is to be assigned the leading place. The position occupied by the thiacyanine dyes is reflected in the relevant journal, patent, and monographic literature. However, this applies only to the various types of symmetrical thiacyanine, in which identical basic residues derived from thiazole are to be found at the ends of the polymethine chain. With regard to the unsymmetrical quinothiacyanines, they form the subject of a relatively few sporadic investigations. This is to be attributed to the fact that they are much more difficult to synthesize than the symmetrical dyes.

Kiprianov and Pilyugin have described a number of quinothiacyanines prepared from a benzothiazole intermediate product in conjunction with quinoline derivatives [3]. Unsymmetrical dyes containing a quinoline system having an aryl radical on the hetero nitrogen have been hitherto unknown in chemistry and are described by us for the first time [4]. In this group of quinothiacyanines of general formula



where Ar = C_6H_5; $C_6H_4CH_3$ (o,p); $C_{10}H_7$ (α,β); X = ClO_4, I, we have synthesized a number of dyes. A study of the effect of the aryls attached to the hetero nitrogen atom on the color of the unsymmetrical quinothiacarbocyanines presented some interest.

The structures of the unsymmetrical dyes that we have synthesized are presented in the table, where there are given also the optical data for the corresponding symmetrical dyes.

Introduction of phenyl in place of ethyl on the hetero nitrogen atom of an unsymmetrical quinothiacarbocyanine resulted in a shift in the absorption maximum towards the red end of the spectrum of 65 mμ. Introduction of a methyl group into the unsymmetrical molecule resulted in an insignificant bathochromic shift (1-2 mμ, No. 2 and 3). The presence of a methyl group in the benzene nucleus and, simultaneously, of a fused benzene ring in the substituent on the hetero nitrogen atom caused a bathochromic shift of 8 mμ in the absorption maximum (No. 4).

As has been noted previously, fusion of the same ring on the benzene nucleus leads to a bathochromic shift in the absorption maximum of 8-11 mμ (No.5,6,8), while fusion to the substituent on the hetero nitrogen leads to a considerably smaller shift (4 mμ). The simultaneous addition of two fused benzene rings to the molecule, one on the benzene nucleus and one on the substituent at the hetero nitrogen, leads to a shift of 14 mμ towards the longer waves.

EXPERIMENTAL

[2-(1-Phenylquinoline)][2-(3-ethylbenzothiazole)] trimethinecyanine perchlorate. 3-Ethyl-2-(2-N-phenylacetamidovinyl)benzothiazolium iodide (0.52 g), 1-phenylquinaldinium perchlorate (0.35 g),

TABLE

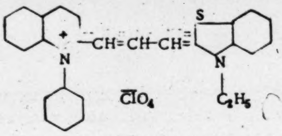
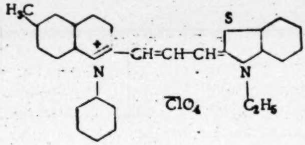
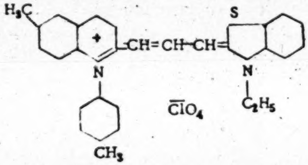
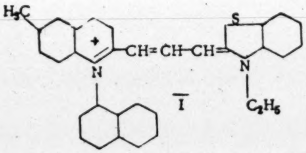
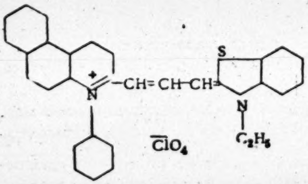
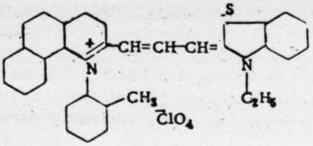
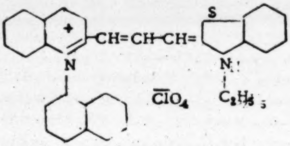
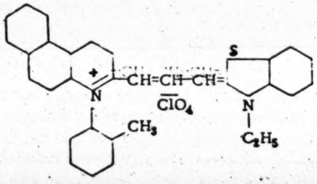
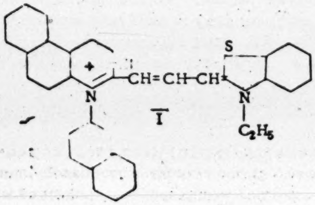
No.	Formula of dye	Absorption max. (mμ)				Shift from additive		$E_{max}\cdot 10^{-4}$
	I II	Symmetrical from I	Symmetrical from II	Unsymmetrical calcd. $\frac{I+II}{2}$	Unsymmetrical (found)	hypsochromic	bathochromic	
1		614	558	586	586	–	–	13.1
2		620	558	589	587	2	–	13.3
3		622	558	590	588	2	–	13.9
4		625	558	591.5	594	–	2.5	13.7
5		645	558	601.5	596	5.5	–	14.8

TABLE (Continued)

No.	Formula of dye I II	Absorption max. (mμ) Symmetrical from I	 Symmetrical from II	 Unsymmetrical calcd. $\frac{I+II}{2}$	 Unsymmetrical (found)	Shift from additive hypsochromic	 bathochromic	$E_{max} \cdot 10^{-4}$
6		642	558	600	597	3	–	13.2
7		618	558	588	590	–	2	12.2
8		644	558	601	594	7	–	13.8
9		654	558	606	600	6	–	14.2

and pyridine (2 ml) were boiled together for 40 min. The dye was precipitated from the pyridine solution with aqueous alcohol and was purified by recrystallization from alcohol. Glistening blue needles (0.2 g, 42.54%), m.p. 256-257° (decomp.). Absorption maximum 586 mμ.

Found %: Cl 7.25

$C_{27}H_{23}N_2ClO_4$. Calculated %: Cl 6.99

[2-(6-Methyl-1-phenylquinoline)][2-(3-ethylbenzothiazole)]trimethinecyanine perchlorate. The quaternary salt from 2,6-dimethyl-1-phenylquinoline (0.2 g) and the 2-methylbenzothiazole intermediate product (0.24 g) were placed in a 25-ml flask, and pyridine (3 ml) and a few drops of acetic anhydride were added. The contents of the flask were heated for 40 min with frequent shaking. The mixture was cooled, and the dye was precipitated with ether and dissolved in a small amount of alcohol. The dye precipitated from the cooled solution; it was filtered off and washed with alcohol and ether. Recrystallization yielded a dark-blue crystalline powder having a metallic luster (0.09 g, 34.6%), m.p. 270° (decomp). Absorption maximum of the dye: 587 mμ.

Found %: Cl 7.72

$C_{28}H_{25}N_2ClO_4$. Calculated %: Cl 7.64

[2-(6-Methyl-1-p-tolylquinoline)][2-(3-ethylbenzothiazole)]trimethinecyanine perchlorate. The quaternary salt (0.4 g, 1.2 mol), the 2-methylbenzothiazole intermediate product (0.4 g, 1 mol), and pyridine (3 ml) were placed in a flask fitted with a reflux condenser and were boiled together continuously for 40 min. The dye was precipitated with ether and then dissolved in alcohol (1 ml). Crystallization was induced by scratching with a glass rod; the crystals were filtered off and washed with alcohol and ether. The dye, after recrystallization from aqueous alcohol, melted at 232-234° (decomp.) (0.2 g, 35%). Absorption maximum of dye: 588 mμ.

Found %: Cl 6.10

$C_{29}H_{27}N_2ClO_4$. Calculated %: Cl 6.45

[2-(6-methyl-1-(1-naphthyl)quinoline)][2-(3-ethylbenzothiazole)]trimethinecyanine iodide. 2,6-Dimethyl-1-(1-naphthyl)quinolinium iodide (0.25 g), the benzothiazole intermediate product (0.15 g), and pyridine (2 ml) were heated together with addition of a few drops of acetic anhydride for 40 min under reflux. On boiling, the reaction mixture took up a stable bluish-violet color. The mixture was cooled and treated with ether. The precipitate was dissolved in alcohol, and the solution obtained was left overnight. The fine crystals that formed were filtered off and washed with ether. The alcoholic solution of the dye is bluish violet. The dye, after recrystallization from aqueous alcohol, melted at 233° (decomp.) (0.06 g, 38%). Absorption maximum of the dye: 594 mμ.

Found %: I 20.88

$C_{32}H_{27}N_2I$. Calculated %: I 21.23

[3-(4-Phenylbenzo/f/quinoline)][2-(3-ethylbenzothiazole)]trimethinecyanine perchlorate. 3-Methyl-4-phenylbenzo/f/quinolinium perchlorate (0.22 g), the 2-methylbenzothiazole intermediate product (0.16 g), pyridine (2 ml), and a few drops of acetic anhydride were boiled together for 1 hr with frequent shaking. The mixture was cooled and the unsymmetrical dye was precipitated by addition of a small amount of ether. It was dissolved in alcohol (2 ml) and precipitated by addition of a saturated solution of potassium perchlorate followed by addition of water (10 ml) and boiling. The finely crystalline precipitate of dye was filtered off, washed with ether, alcohol, and water, and recrystallized from aqueous alcohol (0.09 g, 32%). The cyanine condensation was repeated several times in order to obtain sufficient dye for further investigations. The dye had a m.p. of 220° (decomp) and absorption maximum of 596 mμ.

Found %: Cl 6.19

$C_{31}H_{25}N_2ClO_4$. Calculated %: Cl 6.37

[2-(1-o-Tolylbenzo/h/quinoline)][2-(3-ethylbenzothiazole)]trimethinecyanine perchlorate. 2-Methyl-1-o-tolylbenzo/h/quinolinium perchlorate (0.3 g), the 2-methylbenzothiazole intermediate product (0.15 g), pyridine (3 ml), and a few drops of acetic anhydride were placed in a flask fitted with reflux condenser and boiled together over an asbestos gauze for 50 min. As heating continued, the bluish-lilac color of the reaction mixture became more and more intense. When the mixture was cool, the dye did not come out in a crystalline form, and it was therefore precipitated by addition of a small amount of ether. The precipitate formed was dissolved in alcohol (1 ml) to which, at the boil, a saturated solution of potassium perchlorate was added. The finely crystalline dye was filtered off and washed with water, alcohol, and ether. The dye was recrystallized from aqueous alcohol (0.1 g, 22%). It had m.p. 227° (decomp) and absorption maximum 597 mμ.

Found %: Cl 6.08

$C_{32}H_{27}N_2ClO_4$. Calculated %: Cl 6.22

[2-(1-(1-Naphthyl)quinoline)][2-(3-ethylbenzothiazole)]trimethinecyanine perchlorate. 1-(1-Naphthyl)quinaldinium perchlorate (0.2 g), the 2-methylbenzothiazole intermediate product (0.24 g), pyridine (3 ml), and acetic anhydride (2 drops) were placed in a flask and heated at the boil over an asbestos gauze for 40 min. When the solution had cooled, the dye was separated by addition of ether (5 ml); it was filtered off and was recrystallized from aqueous alcohol (0.08 g, 32.2%). The dye is a dark-blue crystalline powder having a metallic luster, m.p. 228° (decomp). The absorption maximum of the dye is 590 mμ.

Found %: Cl 6.22
$C_{21}H_{25}N_2ClO_4$. Calculated %: Cl 6.37

[3-(4-o-Tolylbenzo/f/quinoline)][2-(3-ethylbenzothiazole)]trimethinecyanine perchlorate. 3-Methyl-4-o-tolylbenzo/f/quinolinium iodide (0.2 g), 3-ethyl-2-(N-phenylacetamidovinyl)-benzothiazolium iodide (0.15 g), pyridine (2.5 ml), and acetic anhydride (2 drops) were heated together at the boil for 50 min in a flask fitted with reflux condenser. When the mixture had cooled, the dye was precipitated with ether and then dissolved in alcohol (2 ml); a saturated solution of potassium perchlorate (2 ml)was added, and the mixture was heated to the boil. On the next day the finely crystalline precipitate of dye was filtered off, washed with ether and alcohol, and recrystallized from aqueous alcohol (0.085 g, 31.4%). The dye was in the form of dark-violet crystals having a metallic luster, m.p. 215°. Absorption maximum 594 mμ.

Found %: Cl 6.16
$C_{32}H_{27}N_2ClO_4$. Calculated %: Cl 6.22

[3-(4-(2-Naphthyl)benzo/f/quinoline)][2-(3-ethylbenzothiazole)]trimethine-cyanine iodide. The benzothiazole intermediate product (0.4 g), the quaternary salt (0.49 g), pyridine (2 ml), and acetic anhydride (0.5 ml) were placed in a flask fitted with reflux condenser and boiled gently for 40 min. As heating proceeded, the contents of the flask acquired a bluish-green color with a reddish tinge.. When the mixture had cooled, the dye was precipitated with ether and filtered off after being converted into the solid state by intermediate dissolution in a small amount of alcohol. The dye was recrystallized from aqueous alcohol (0.22 g, 40.7%). M.p. 250° (decomp.). The absorption curve of a solution of the dye in ethanol was determined; absorption maximum: 600 mμ.

Found %: I 19.88
$C_{35}H_{27}N_2I$. Calculated %: I 20.03

I express my sincere thanks to V. N. Tolmachev, senior scientific worker in the Institute of Chemistry of the Kharkov State University, for help in the determination of absorption spectra.

SUMMARY

1. Nine new quinothiacarbocyanines have been prepared containing aryl radicals on the hetero nitrogen of quinoline.

2. It has been shown that replacement of ethyl on the hetero nitrogen atom by phenyl or naphthyl leads to a slight bathochromic shift in the absorption maximum of the dye.

3. The absorption maxima of the quinothiacarbocyanines obtained may be derived by an additive relationship from those of the corresponding symmetrical dyes, but the intensity of the absorption is reduced in comparison with that of the corresponding symmetrical dyes.

Received December 1, 1951

Institute of Organic Chemistry of the
USSR Academy of Sciences
Chernovitsy State University

LITERATURE CITED

[1] G. Williams, Jahresber., 1856, 536.

[2] W. H. Mills. J. Chem. Soc. 121,455 (1922).

[3] A. I. Kiprianov and G. T. Pilyugin. Sci. Mem. Kharkov State Univ. No. 10, 104 (1937).

[4] G. T. Pilyugin. Bull. Acad. Sci. USSR. Div. Chem. Sci., No. 2, 353 (1952)*; G. T. Pilyugin and Z. Ya. Krayner. Proc. Acad. Sci. USSR, 81, 4, 609 (1951).

---

* See Consultants Bureau English Translation, p. 347.

BLANK
PAGE

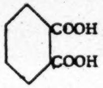
MACROMOLECULAR COMPOUNDS

COMMUNICATION 44. POLYESTERS OF CERTAIN AROMATIC DICARBOXYLIC ACIDS

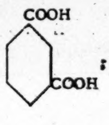
V. V. Korshak and T. A. Soboleva

Polyesters derived from glycols and aromatic dicarboxylic acids have as yet received very little investigation. There are only a few papers in the literature that are devoted to the study of such compounds [1]. Thus, Drinberg, Snedze, and Neohaeva [2] studied the polycondensation of diphenic acid with glycerol and described the properties of the polyesters formed. Polyethylene diphenate was described also by Carothers and Arvin [3].

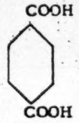
The object of the present investigation was to determine the effect on the properties of the polyester of the structure of the aromatic dicarboxylic acid, particularly with respect to the relative positions of the carboxyl groups and to the number of aromatic nuclei, and to elucidate also the part played by the methyl ne groups separating these nuclei. For this purpose we have prepared polyesters by the condensation of glycols (ethylene glycol and diethylene glycol) with aromatic dicarboxylic acids having either one nucleus, e.g. phthalic (I), isophthalic (II), terephthalic (III), or two nuclei: diphenic (IV) and 4,4'-biphenyldicarboxylic (V). Also, acids having one or two methylene groups situated between aromatic nuclei were taken: 4,4'-methylenedibenzoic acid (VI) and α,α'-bi-p-toluic acid (VII):



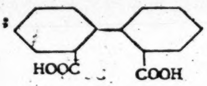
(I)



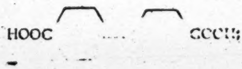
(II)



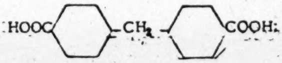
(III)



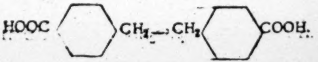
(IV)



(V)



(VI)



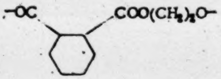
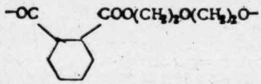
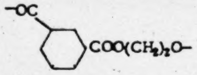
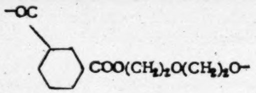
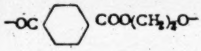
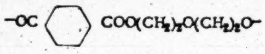
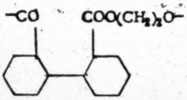
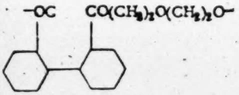
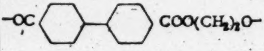
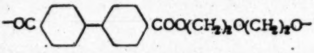
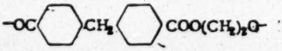
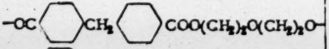
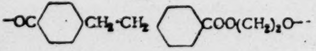
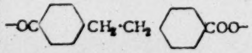
(VII)

From these acids a number of polyesters were prepared. Their properties are given in the table.

In solvents such as acetic acid, acetone, strong hydrochloric acid, and aqueous caustic soda all the polyesters enumerated in the table are insoluble with the exception of the ethylene glycol and diethylene glycol esters of diphenic acid, which dissolve in hot acetic acid. As will be seen from the table, the properties of the polyesters vary in regular fashion when one glycol or acid is changed for another. All the ethylene glycol esters are solids having melting points higher than those of the diethylene glycol esters. The latter are sometimes liquid at room temperature, (polyester of phthalic acid) or are rubberlike (polyester of terephthalic acid). In this case there is manifested the specific effect of the ether linkage in the diethylene glycol residue; this confers a high flexibility on the polyester chain, which is expressed in the lower melting point and in the appearance of rubberlike properties. That the cause in this case is the ether linkage may be shown by a comparison of polydiglycol terephthalate with polypentamethylene terephthalate [4].

The effect of the structure of the dicarboxylic acid on the properties of the polyester is still greater. Thus, in the case of the isomeric benzenedicarboxylic acids the properties of the polyesters change fundamentally with change in the relative positions of the carboxyl groups. As we proceed in order from the ortho to the meta and para isomers, the melting point rises both for the ethylene glycol polyesters (92-104, 102-108, 250-256° respectively)

TABLE

No.	Repeating unit	Appearance of polyester	M.p.°C	Solubility in					
				dioxane	chloroform	alcohol	benzene	cresol	sulfuric acid
1	 —OC COO(CH₂)₂O—	solid	92-104	x	x	—	—	+	+
2	 —OC COO(CH₂)₂O(CH₂)₂O—	like petroleum jelly	sirup	x	x	—	x	+	+
3	 —OC COO(CH₂)₂O—	solid	102-108	—	—	—	—	x	+
4	 —OC COO(CH₂)₂O(CH₂)₂O—	"	85-90	—	—	—	—	x	+
5	 —OC COO(CH₂)₂O—	"	256	—	—	—	—	x	x
6	 —OC COO(CH₂)₂O(CH₂)₂O—	rubber-like	125-139	—	+	—	—	x	x
7	 —CO COO(CH₂)₂O—	brittle solid	110-130	x	x	—	x	x	+
8	 —OC CO(CH₂)₂O(CH₂)₂O—	solid	80-95	—	—	—	x	x	+
9	 —OC COO(CH₂)₂O—	"	not melted below 320°	—	—	—	—	—	x
10	 —OC COO(CH₂)₂O(CH₂)₂O—	"	159-170	—	—	—	—	x	x
11	 —OC CH₂ COO(CH₂)₂O—	"	not melted below 320°	—	—	—	—	—	x
12	 —OC CH₂ COO(CH₂)₂O(CH₂)₂O—	"	126-145	x	x	—	—	x	x
13	 —OC CH₂·CH₂ COO(CH₂)₂O—	"	not melted below 320°	—	—	—	—	—	x
14	 —OC CH₂·CH₂ COO—	"	85-105	—	—	—	—	x	x

$-(CH_2)_2O(CH_2)_2O-$

NOTE. The sign — indicates insoluble, + indicates soluble at room temperature, x indicates soluble on warming.

and for the diethylene glycol polyesters (like petroleum jelly, 85-90, 125-139° respectively). It is interesting to note that a similar picture is to be observed also for the biphenyldicarboxylic acids: the polyesters of the para acid melt higher than the polyesters of the ortho acid, both for ethylene glycol (m.p. 110-130° and above 320° respectively), and also for diethylene glycol (m.p. 70-95° and 159-170° respectively).

Also, the effect should be noted of the number of benzene nuclei and of their relative disposition. Polyesters from a biphenyldicarboxylic acid have higher melting points than polyesters from the corresponding benzenedicarboxylic acids. Thus for the polyesters from ortho- and para-dicarboxylic acids and a) ethylene glycol the melting points are respectively 92-104° and 110-130° (benzenedicarboxylic), 250-256°, higher than 320° (biphenyldicarboxylic), while for the polyesters with b) diethylene glycol we have: sirup, m.p. 70-95° (benzenedicarboxylic), m.p. 125-139°, 159-170° (biphenyldicarboxylic). This is the picture when the phenyl groups adjoin.

If, however, dicarboxylic acids are taken in which the two phenyl groups are separated by one or by two methylene groups, the melting points of the polyesters are lowered in comparison with those of the biphenyldicarboxylic derivatives; thus in the case of the polyesters from diethylene glycol: m.p. respectively 159-170°, 126-145°, 85-105°

With regard to the effect of the structure of the acid on the solubility of the polyester, an equally clear picture is to be observed. The polyesters from diethylene glycol are generally more readily soluble than those from ethylene glycol. Polyesters from p-dicarboxylic acids are less soluble than those from m- or o-acids. Polyesters derived from dicarboxylic acids containing two benzene nuclei substituted in the p-positions are distinguished by particularly poor solubility. Some of them are soluble only in strong sulfuric acid on warming, when it is possible that hydrolytic breakdown takes place. In the other solvents they do not dissolve, being similar to three-dimensional polymers in this respect.

The Properties of Three-dimensional Polymers

Until comparatively recently it has been considered axiomatic that three-dimensional macromolecular compounds are distinguished from linear compounds of this type by their complete insolubility and inability to melt when heated [5]. We consider that the cause of these differences is that three-dimensional macromolecular compounds consist essentially of linear chains knit together by a greater or smaller number of cross-links. Owing to the presence of these chemical cross-links, the linear chains cannot be separated from one another either by solvation forces or by moderate thermal action, for the energies of these linkages are too great to be overcome by forces arising from the action of solvents or of moderate heating. Sometimes, if the number of cross-links is not high, swelling occurs in the three-dimensional structure owing to the intrusion of solvent between the polymer molecules. However, this swelling does not lead finally to dissolution, but amounts essentially to the absorption of a large amount of solvent. In the case of such three-dimensional polymers, moderate heating leads generally to softening, but not to melting.

Macromolecular compounds, both three-dimensional and linear, undergo destruction at high temperatures as a result of pyrolysis; this occurs when the energy of the thermal movements of the molecules begins to exceed the energies of the chemical bonds. However, such concepts and definitions are beginning to come more and more into conflict with the experimental facts. Quite a few macromolecular compounds have been synthesized recently which undoubtedly belong to the class of linear polymers, but have properties that are characteristic of three-dimensional compounds. Examples of such substances are to be found in the polyamides prepared by us from adipic or sebacic acid and diamines such as benzidine [6] or α,α'-bi-p-toluidine [7], also in the series of polyesters formed between ethylene glycol or diethylene glycol and aromatic dicarboxylic acids, described in this paper; also, polymers such as polyvinylidene chloride [8], polytetrafluoroethylene [9], and, probably, urea-formaldehyde resin [10].

In the molecules of these polymers, cross-links are absent, but the polymers are insoluble in all solvents and do not melt when heated (they decompose at high temperatures). Consequently, in their properties they correspond to three-dimensional compounds. The cause of this phenomenon is to be found in the large number of polar groups, such as amide or phenylene, and of such atoms as chlorine or fluorine that are contained in the macromolecules of the compounds enumerated. Also, their chains are notable for their tendency to become close-packed, which is expressed by an X-radiogram corresponding to a high content of orderly crystalline substance. Owing to the presence of these polar groups, the usually rather weak Van der Waals forces between the chains become considerable, and hence the binding force of one chain to another attains high values. The magnitude of these forces, evidently, can in a number of cases attain the same value as the forces in the primary chemical of bonds in three-dimensional polymers. Hence, such macromolecular compounds acquire properties that are typical for three-dimensional polymers; they do not dissolve and do not melt [illegible]

This conclusion is confirmed by the fact that when the amide hydrogen atoms of polyamides are replaced by methyl groups readily soluble rubberlike polyamides are obtained [11]; for the formation of hydrogen bonds between the individual polyamide chains, which determine the great force that binds the individual chains to one another, does not now occur. Another example is the copolymer of vinylidene chloride with vinyl chloride. In this copolymer, the residues of the two original substances are not disposed in a regular fashion, and it is difficult for an orderly arrangement to be attained. Hence, this copolymer dissolves and melts more readily than polyvinylidene chloride.

On the basis of the above we may conclude that absence of an ability to dissolve and to melt is not always a proof of a three-dimensional structure; it may be an attribute also of linear polymers when polar groups are present and there is a tendency to take up an ordered arrangement.

The polyesters that we have prepared from dicarboxylic acids containing two benzene nuclei are insoluble in all organic and inorganic solvents, apart from strong sulfuric acid. Thus, in this respect they resemble three-dimensional polymers. However, this resemblance is purely formal, for there is no doubt that we are concerned here with linear polymers. The reason for the lack of solubility is evidently connected with the presence of fairly high binding forces between the benzene nuclei of individual chains. As is well known, the benzene ring contains six π-electrons, which are distributed within the nucleus and are energetically not fully saturated; their orbitals are disposed perpendicularly to the plane of the ring, and it is evident that their interaction results in the appearance of large mutual forces between these nuclei.

SUMMARY

1. Polyesters have been prepared by the condensation of ethylene glycol and diethylene glycol with aromatic dicarboxylic acids.

2. The question of the effect of the structure of the polymer chain on the physical properties of the polymer has been examined.

3. It has been shown that generally held views concerning three-dimensional polymers require modification.

4. The properties of the polyesters obtained have been demonstrated.

Received September 29, 1950

Institute of Organic Chemistry of the
USSR Academy of Sciences

LITERATURE CITED

[1] J. H. Whinfield, Nature 158, 930 (1946).
[2] A. Ya. Drinberg, A. A. Snedze, and L. P. Nechaeva. Proc. Leningrad Tech. Inst. No. 14, 98 (1947).
[3] W. H. Carothers, C. A. Arvin, J. Am. Chem. Soc. 51, 2560 (1929).
[4] R. Hill, E. E. Walker, J. Polymer Science 3, 609 (1948).
[5] V. V. Korshak and S. R. Rafikov. Synthesis and Investigation of Macromolecular Compounds. Acad. Sci. USSR Press. Moscow-Leningrad 1949, p. 22.
[6] V. V. Korshak and S. R. Rafikov. J. Gen. Chem. 14, 974 (1944).
[7] V. V. Korshak and S. V. Rogozhin. Bull. Acad. Sci. USSR. Div. Chem. Sci. 593 (1951).
[8] I. P. Losev and E. B. Trostyanskaya. Prog. Chem., 5, 395 (1945).
[9] A. I. Lazarev and M. F. Sorokin. J. Chem. Ind. No. 5, 20 (1947).
[10] V. V. Korshak. Chemistry of Macromolecular Compounds, Acad. Sci. USSR Press. Moscow-Leningrad. 1950, p 481.
[11] R. Simha, Ann. N. Y. Acad. Sci. 44, 297 (1943).

MACROMOLECULAR COMPOUNDS

COMMUNICATION 45. SIGNIFICANCE OF THE DECARBOXYLATION OF DICARBOXYLIC ACIDS IN THE POLYCONDENSATION PROCESS

V. V. Korshak and S. V. Rogozhin

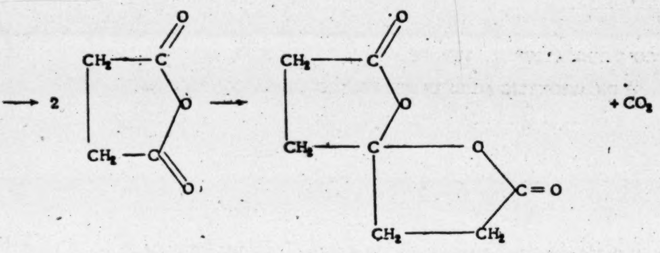
In the chemistry of macromolecular compounds the process of polymer formation by the polycondensation of bifunctional compounds is usually broken down into three fundamental stages: 1) beginning of chain growth, 2) chain growth, and 3) curtailment of chain growth.

The laws of the first two stages of the process have received a fair degree of study and development in a number of papers [1,2], but the causes leading to termination of chain growth have still not been fully elucidated. It has been found that, owing to the equilibrium nature of the polycondensation process, the molecular weight of the polymer, i.e., its chain length, is greatly affected by the ratio of components [3] and by the possibility of various chemical reactions at the terminal functional groups, leading to breaking of the chain [4].

The occurrence of chemical reactions at the terminal functional groups has been established in a number of investigations [5]. One of us with Zamyatina has observed that in the polycondensation of 1,6-hexanediamine with adipic acid the splitting-off of carbon dioxide from the adipic acid occurs [6]. The significance of such chemical changes, which lead to the destruction of the reacting end-groups, is particularly great in the preparation of linear polymers by condensation of bifunctional compounds. The determination of the effect of temperature on the thermal stability of dicarboxylic acids presents undoubted interest in connection with the possibility of decarboxylation during the course of polycondensation, but systematic investigations of this kind have not yet been carried out, and only isolated results are to be found in the literature. It is known, for example, that the presence in the molecule of a dicarboxylic acid of two carboxyl groups, which have a negative character, greatly increases the tendency to undergo decomposition. It is obvious that this effect will be most prominent among the first members of the homologous series of dicarboxylic acids owing to the mutual proximity of the carboxyl groups.

Actually, on being heated, oxalic acid yields carbon dioxide and formic acid [7]. It has been found that the reaction proceeds particularly rapidly at above 170°. The rate of decomposition increases in presence of water. Malonic acid decomposes more readily than oxalic acid. On being heated to 140°, malonic acid loses carbon dioxide and is converted into acetic acid [8]. This change occurs below 70° in aqueous solution [9]. The majority of the homologs of malonic acid decompose in the range 160-180°. When the fatty acids, and particularly their salts, are decomposed, ketones formed from the two acid residues are the main decomposition products. In the case of dicarboxylic acids, it is necessary to take into account the possibility of the formation of anhydrides and of cyclic ketones. Anhydride formation may proceed also by the splitting of water from two molecules of acid and may lead to formation of linear polyanhydrides of high molecular weight.

Investigations of Carothers and Hill [10] showed that in these reactions five- and six-membered rings were the most readily formed. When the structural unit contains 7-15 members, dimeric cyclic products or linear polymers are often formed. Thus, succinic acid, on being heated, readily forms an anhydride having a five-membered ring [11], which, on being heated further, is slowly converted by the splitting-off of one molecule of carbon dioxide from two molecules of the anhydride into the dilactone of γ-oxopimelic (hydrochelidonic) acid.



Glutaric acid rapidly distils with slight decomposition at below 300°. When it is distilled slowly, a mixture of acids and anhydrides is formed. Cyclopentanone is readily formed by the action of heat on salts of adipic acid. Aschan [12] found that cyclopentanone is formed when adipic acid is heated in presence of carbon dioxide. Blank [13] prepared cyclopentanone in 50% yield by heating adipic anhydride. Very little is known concerning the pyrolysis of the higher dicarboxylic acids. It is known that the presence of various catalysts greatly reduces the decomposition temperature.

EXPERIMENTAL

All the investigations reported in the literature on the decomposition of organic acids are based on chemical methods of investigating the decomposition products. In a number of investigations, the kinetics of decomposition have been determined from the change in the acid value [14], for which a considerable amount of substance, and also of time, is required for the performance of the investigation.

The method that we have developed presents the possibility of following continuously the course of the decomposition of acids, and an insignificant amount of material is required for the investigation. A weighed amount of the substance under investigation contained in a small tube is placed in a bath of Wood's metal. The tube is connected by narrow rubber tubing to a measuring system, which is contained in a thermostat; the temperature of the liquid in this thermostat is maintained constant within ± 0.05° by the aid of a Hoppler thermostat. The volume of the measuring system, tubing, and reaction tube is measured accurately. The gaseous decomposition products alter the pressure in the system, the changes in pressure being determined by the aid of the water and mercury manometers that form part of the measuring system. The course of the decomposition can be judged from the rate at which the pressure changes. The arrangement is shown diagrammatically in Figure 1. (See plate, page 547-a).

The calculation of the volume of carbon dioxide evolved and of the percentage decomposition of the acid under investigation is based on the excess pressure in the system, on the results of measurement of the volume of the system of manometric tubes, and on the fundamental law of the kinetic theory of gases:

$$\frac{p_0 V_0}{T_0} = \frac{p_1 V_1}{T_1}$$

The correctness of the formulas was verified by determining the percentage of decomposition of the acid by titration of the undecomposed acid. For all experiments on the decomposition of oxalic and malonic acids agreeing results were obtained.

The volume of carbon dioxide evolved was calculated for our experimental arrangement by the formulas:

$$\Delta V = \frac{273\Delta p}{760T}\left[V_s' + 0.01073\left(p_{at} + \frac{\Delta p}{13.6}\right)\right]$$

or

$$\Delta V = \frac{273\Delta' p}{760T}[V_s' + 0.146(p_{at} + \Delta' p)].$$

When the water manometer is cut out

$$\Delta V = \frac{273\Delta' p}{760T}[V_s' + 0.01(p_{at} + \Delta' p)],$$

where $\underline{\Delta p}$ is the excess pressure in mm water, $\underline{\Delta' p}$ is the excess pressure in mm Hg, P_{at} is the atmospheric pressure in mm Hg., V_s' is the volume of the system (ml) at atmospheric pressure, $\underline{T}$ is the temperature of the thermostat liquid in °K.

The percentage decomposition of the acid is

$$2.232 \cdot 10^{-3}\frac{M \cdot \Delta V}{n},$$

where $\underline{M}$ is the molecular weight of the acid, $\underline{\Delta V}$ is the volume of carbon dioxide evolved, and $\underline{n}$ is the amount of acid (g).

For monocarboxylic acids the coefficient is doubled.

EXPERIMENTAL PROCEDURE

A weighed amount (0.2-1.0 g) of the substance is placed in the tube, which is inserted into its jacket, through which water from the Höppler thermostat is flowing; in this way the temperature conditions throughout practically the whole of the reaction tube are made the same as those in the rest of the system. The tube is connected to the system with rubber tubing, and the tap that connects the whole system to the atmosphere is opened. The tube with its connecting tubing is placed in a thermostated vessel and kept there for 10 minutes; the temperature of the air in the system should then be equal to the temperature of the thermostat liquid. The tap connecting the system to the atmosphere is closed, and the reaction tube is placed in the bath of Wood's metal. The temperature of the bath is varied by the aid of a contact thermometer and a relay, or it is maintained constant within ±0.5°. At definite intervals of time at constant decomposition temperature, or at definite intervals of temperature when the temperature is varied, the excess pressure is read on the water manometer, if it is low, or on the mercury manometer, if it is high. When decomposition is complete, the tube is again placed in the thermostat and kept there for 10 minutes. The excess pressure is read for an air temperature equal to the temperature of the thermostat; from this the extent of the decomposition of the acid can be determined.

EXPERIMENTAL RESULTS

The results obtained by this method are given in Tables 1 and 2. In order that the various acids may be compared, the measured excess pressure has been recalculated for 1 mole of acid.

The residual pressure in the case of oxalic acid was 306 mm Hg, and the percentage of acid decomposed was: a) (calculated from residual pressure) 31.2; b) (calculated from titration results) 31.1.

In the case of malonic acid the residual pressure was 205 mm Hg, whence we obtain 21.6% decomposed acid (by titration, 21.2%).

It will be seen from the results in Tables 1 and 2 and in Figure 2 that with increase in the molecular weight of the acid the thermal stability increases. The first members of the homologous series are notable for their insignificant thermal stability and differ greatly in their behavior from the remaining dicarboxylic acids. It will be seen that, judging from the behavior of malonic, glutaric, and azelaic acids, acids containing an odd number of carbon atoms decompose more readily than the adjacent members, which have an even number of carbon atoms.

TABLE 1

Acid	Oxalic		Malonic	
Molecular Weight	90		104	
Amount taken, g	0.3808		0.4318	
Pressure mm Hg / Temperature, °C	p	$\frac{p \cdot M}{m}$	p	$\frac{p \cdot M}{m}$
100	0-2	60	0-2	160
110	0-2	120	0-2	320
120	0-2	180	2	480
130	1	240	6	1 400
140	2	470	18	4 300
150	10	2 400	98	24 000
160	36	8 500	166	40 000
170	130	31 000	210	51 000
180	320	76 000		

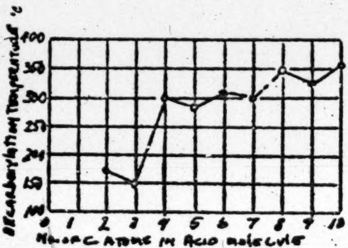


Fig. 3. Variation in decarboxylation temperature of dicarboxylic acids with the number of carbon atoms in the acid molecule.

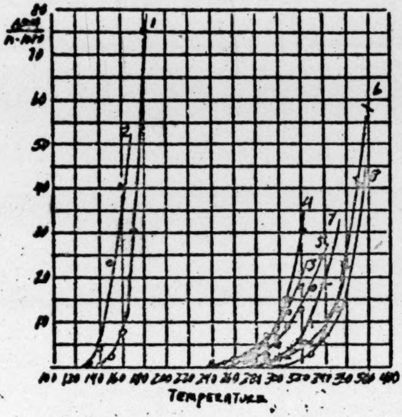


Fig. 2. Decomposition of dicarboxylic acids: 1) oxalic; 2) malonic; 3) succinic; 4) glutaric; 5) adipic; 6) suberic; 7) azelaic; 8) sebacic.

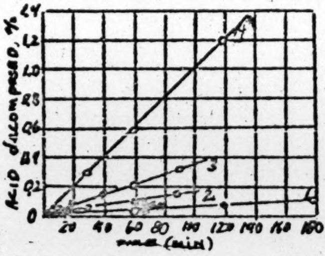


Fig. 4. Dependence of rate of decomposition of adipic acid on temperature. 1) 250°; 2) 260°; 3) 270° and 4) 280°.

Each acid decomposes most vigorously on reaching a definite temperature, which may be termed the decarboxylation temperature.

Decarboxylation temperatures of the acids investigated are given in Table 3.

The variation in the decarboxylation temperature with increase in the chain length of the dicarboxylic acid is shown in Figure 3. The experiments carried out at constant temperature permit a more exact estimate of the temperature below which no appreciable decomposition is observed. It was established that in the case of adipic acid there was no appreciable decomposition at below 240° (Table 4).

The results obtained on the decomposition of adipic acid at constant temperatures enable us to make an estimate of the variation of reaction rate with temperature. Since the slope of the straight line (Figure 4) is determined by the rate of reaction, the variation of tgα with temperature gives the variation of reaction rate with temperature:

1) 250° tgα_1 = 0.044
2) 260° tgα_2 = 0.13
3) 270° tgα_3 = 0.356
4) 280° tgα_4 = 1.0

TABLE 2

Acid	Succinic		Glutaric		Adipic		Suberic		Azelaic		Sebacic	
Molecular Wt.	118		132		146		174		188		202	
Amount taken, g	0.4659		0.1580		0.3850		0.2932		0.3148		0.3234	
Pressure in mm Hg / Temperature °C	p	$\frac{p\cdot M}{m}$	p	$\frac{p\cdot M}{m}$	p	$\frac{p\cdot M}{m}$	p	$\frac{p\cdot M}{m}$	p	$\frac{p\cdot M}{m}$	p	$\frac{p\cdot M}{m}$
200	1-2	250	–	–	–	–	–	–	–	–	–	–
210	0-2	380	–	–	–	–	–	–	–	–	–	–
220	2	400	–	–	0-2	150	–	–	–	–	–	–
230	3	530	0-2	420	0-2	300	–	–	–	–	–	–
240	3-4	880	0-2	840	0-2	450	–	–	–	–	–	–
250	6-8	1 800	2	1 700	2	600	0-2	300	–	–	–	–
260	10	2 500	2-3	2 100	3	780	0-2	600	–	–	–	–
270	12	3 000	3-4	2 900	4	1 100	0-2	900	0-2	400	–	–
280	16	4 100	4	3 300	6	2 300	2	1 200	0-2	810	0-2	410
290	19	4 900	7	5 800	9	3 800	3	1 800	2	1200	0-2	820
300	28	7 100	13	11 000	15	5 700	4	2 400	4	2 500	2	1 200
310	50	13 000	20	17 000	25	9 500	5	3 000	8	4 900	2	1 200
320	72	18 000	38	32 000	36	14 000	7	4 100	11	6 800	3	1 900
330	–	–	–	–	48	18 000	9	5 300	17	10 000	6	3 700
340	–	–	–	–	66	25 000	12	7 100	32	15 000	10	6 000
350	–	–	–	–	–	–	19	11 000	50	31 000	22	14 000
360	–	–	–	–	–	–	40	29 000	–	–	45	28 000
370	–	–	–	–	–	–	72	43 000	–	–	63	42 000
330	–	–	–	–	–	–	100	59 000	–	–	–	–

TABLE 3

No.	Name of acid	Temp. °C
1	Oxalic	170
2	Malonic	150
3	Succinic	300
4	Glutaric	285
5	Adipic	310
6	Suberic	350
7	Azelaic	330
8	Sebacic	360

TABLE 4

Decomposition temp. 250°		Decomposition temp. 260°		Decomposition temp. 270°		Decomposition temp. 280°	
Duration of decomposition (min.)	% of decomposition	Duration of decomposition (min.)	% of decomposition	Duration of decomposition (min.)	% of decomposition	Duration of decomposition (min.)	% of decomposition
60	0.0272	15	0.0178	10	0.04	30	0.298
120	0.0546	30	0.042	20	0.08	60	0.62
180	0.082	60	0.085	40	0.13	120	1.14
–	–	90	0.129	60	0.20	–	–
–	–	–	–	90	0.31	–	–

The temperature coefficient of the reaction rate is given by a ratio of tangents

$$\frac{\operatorname{tg}\alpha_2}{\operatorname{tg}\alpha_1}=\frac{0.13}{0.044}=2.95;$$

$$\frac{\operatorname{tg}\alpha_3}{\operatorname{tg}\alpha_2}=\frac{0.356}{0.13}=2.75;$$

$$\frac{\operatorname{tg}\alpha_4}{\operatorname{tg}\alpha_3}=\frac{1.0}{0.356}=2.82.$$

The mean value of the coefficient is 2.84.

Oxalic acid behaves in a similar way. It was found that oxalic acid does not decompose appreciably below 110°. The results obtained in the study of the decomposition of the acids at constant temperatures enables us to calculate activation energies, reaction rate constants, and also the orders of the reactions.

The activation energy was calculated from the Van't Hoff-Arrhenius equation

$$\ln\frac{k_1}{k_2}=\frac{A}{R}\left[\frac{1}{T_2}-\frac{1}{T_1}\right]$$

where the values of the tangents may be inserted in place of k_1 and k_2 (see Table 6) The value of the constant calculated from the first-order equation

$$k=\frac{1}{t}\ln\frac{a}{a-k}$$

remains approximately constant, and the decomposition of adipic acid may be regarded as a first-order reaction. The values of k are given in Table 5.

DISCUSSION OF RESULTS

The results we have obtained show that dicarboxylic acids very readily decompose at elevated temperatures, giving carbon dioxide and the corresponding monocarboxylic acid according to the equation:

$$HOOC(CH_2)_nCOOH \rightarrow CH_3(CH_2)_{n-1}COOH + CO_2$$

The monocarboxylic acids formed in the decomposition of oxalic and malonic acids were isolated by us and identified. Formic acid is formed from oxalic, acetic from malonic, etc. This decarboxylation reaction must play an important part in the processes of polycondensation between dicarboxylic acids and other bifunctional compounds. The results that follow from this may be of two kinds. In the first place, as a result of decarboxylation and conversion of dicarboxylic acids into monocarboxylic acids, there is a reduction in the total number of reactive groups, which must lead to a reduction in the molecular weight of the polycondensation products obtained owing to the disturbance in the molecular ratio of the initial substances. Presence of excess of one or other of the initial substances leads to a lowering of the molecular weight of the polycondensation product to an extent that is directly proportional to the excess; this has been shown by one of us on the basis of a large number of examples [15]. In the second place, the monocarboxylic acids formed "close" the end-groups and bring chain growth to a halt, thus lowering the molecular weight of the product formed. Finally, if the polycondensation reaction is proceeding at temperatures higher than the decarboxylation temperature, all possibility, even in principle, of obtaining a macromolecular polycondensation product disappears.

It now becomes clear why acids such as oxalic and malonic do not give macromolecular polyesters and polyamides as the result of polycondensation reactions with glycols and diamines, for they readily decompose at fairly low temperatures.

TABLE 5

Temp. of decomposition of acid (°C)	Duration of decomposition (hr)	% decomposition of acid	$k = \frac{1}{t} \ln \frac{a}{a-x} \cdot 10^{-2}$	Mean value of constant $\cdot 10^{-2}$
250	1.0	0.0272	0.0278	
250	2.0	0.0546	0.0276	0.0276
250	3.0	0.082	0.0275	
260	0.25	0.0178	0.0828	
260	0.5	0.042	0.0856	
260	1.0	0.085	0.0851	
260	1.5	0.129	0.0858	0.0848
260	0.167	0.04	0.241	
260	0.333	0.08	0.241	
260	0.666	0.13	0.1935	
270	1.0	0.20	0.203	0.2277
270	1.5	0.31	0.260	
280	0.5	0.298	0.581	
280	1.0	0.62	0.621	0.5916
280	1.5	1.14	0.573	

TABLE 6

	Temp. intervals (°C)			Mean value
	250-260	260-270	270-280	
1 $\frac{k_{t+10}}{kt}$	3.072	2.685	2.598	2.785
2 $\frac{tg\alpha_{t+10}}{tg\alpha}$	2.95	2.75	2.82	2.84
3 Activation energy calculated from tangent ratio	59 778	58 208	61 600	59 860
4 Activation energy calculated from constants	62 089	56 729	56 893	58 570

SUMMARY

1. A method has been developed for the determination of the thermal stability and decomposition kinetics for organic carboxylic acids.

2. The decarboxylation temperatures have been determined for oxalic, malonic, succinic, glutaric, adipic, suberic, azelaic, and sebacic acids.

3. It has been found that dicarboxylic acids having an odd number of carbon atoms decompose at lower temperatures than acids having an even number of carbon atoms.

4. It has been shown that the thermal stability of the acid increases as we proceed from the lower to the higher members of the homologous series of dicarboxylic acids.

5. It has been shown that decarboxylation of dicarboxylic acids must play a considerable inhibiting role in the course of the polycondensation of these acids with bifunctional substances.

6. On the basis of the results on the thermal decomposition of adipic acid, calculations have been made of reaction order and activation energy.

Received October 20, 1950

Institute of Organic Chemistry of the USSR Academy of Sciences

LITERATURE CITED

[1] V.V.Korshak, S.R.Rafikov, and V.A.Zamyatina. Report of the Sixth Conference on Macromolecular Compounds. USSR Acad.Sci.Press, Moscow-Leningrad (1949), pp. 3-16.

[2] V.V.Korshak, S.R.Rafikov. Synthesis and Investigation of Macromolecular Compounds. USSR Acad. Sci. Press, Moscow-Leningrad (1949), pp. 201-215.

[3] V.V.Korshak, V.V.Golubev, and G.S.Kolesnikov. Investigations on Macromolecular Compounds. USSR Acad. Sci. Press, Moscow-Leningrad (1949), pp. 22-32.

[4] V.V.Korshak. Bull. Acad. Sci. USSR., Div. Chem. Sci., No. 1, 47 (1950).

[5] V.V.Korshak, S.R.Rafikov, and L.N.Pinkina. J. Gen Chem., 14, 1003 (1944); V.V.Korshak, N.N.Lebedev, and M.A.Tsipershtein. J. Gen. Chem., 19, 683 (1949); see Consultants Bureau translation, p. 647.

[6] V.V.Korshak and V.A.Zamyatina. Bull.Acad.Sci.USSR, Div.Chem.Sci., 609 (1945).

[7] Gay-Lussac. Ann., 1, 20 (1832).

[8] C. Heintzel. Ann., 139, 132 (1866).

[9] W. Lameuroux. Compt. rend., 128, 998 (1899).

[10] W. Carothers and H.Hill. J. Am. Chem. Soc., 55, 5023 (1933).

[11] D'Arcet. Ann. Chim., (2), 58, 288 (1835).

[12] O. Aschan. Ber., 45, 1603 (1902).

[13] P. Blank. Compt. rend., 144, 1356 (1907).

[14] R. Willstätter. Ber., 40, 3876 (1907).

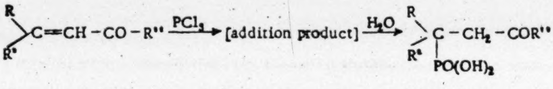
[15] V. V.Korshak and S.R.Rafikov. Proc. Acad. Sci. USSR, 48, 36 (1945); V.V.Korshak and V.V.Golubev. Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 2, 186 (1946); V.V.Korshak, G.S.Kolesnikov, and A.V.Kharchevnikova. Proc.Acad. Sci. USSR, 56, 170 (1947); V.V.Korshak and V.V.Golubev. Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 4, 379 (1949).

BLANK
PAGE

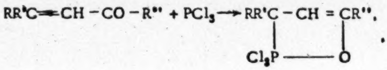
THE REACTION OF PHOSPHORUS TRICHLORIDE WITH UNSATURATED CYCLIC KETONES

M.I.Kabachnik and T.Ya.Medved

α,β-Unsaturated ketones, as is well known, react at room temperature with phosphorus trichloride in a medium of acetic anhydride or of glacial acetic acid with formation of addition products, which are converted by hydrolysis into γ-oxoalkylphosphonic acids [1]:

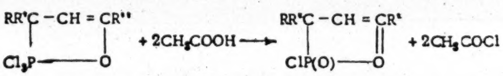


Conant and Cook suggested [2] that the mechanism of the reaction involves 1,4-addition of phosphorus trichloride:


(1)

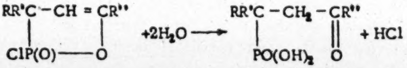
$$RR'C{=}CH-CO-R'' + PCl_3 \longrightarrow \begin{array}{l} RR'C-CH=CR'', \\ \quad | \qquad\qquad\quad | \\ Cl_3P \text{———} O \end{array} \qquad (1)$$

acetolysis of this intermediate product giving the acid chloride (or anhydride) of a 'lactono acid':


(2)

$$\begin{array}{l} RR'C-CH=CR'' \\ \quad | \qquad\qquad\quad | \\ Cl_3P \text{———} O \end{array} + 2CH_3COOH \longrightarrow \begin{array}{l} RR'C-CH=CR' \\ \quad | \qquad\qquad\quad \| \\ ClP(O) \text{——} O \end{array} + 2CH_3COCl \qquad (2)$$

and finally hydrolysis of this acid chloride (or anhydride);

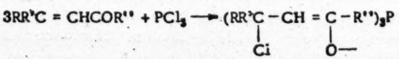

(3)

$$\begin{array}{l} RR'C-CH=CR'' \\ \quad | \qquad\qquad\quad | \\ ClP(O) \text{——} O \end{array} + 2H_2O \longrightarrow \begin{array}{l} RR'C-CH_2-CR'' \\ \quad | \qquad\qquad\quad \| \\ PO(OH)_2 \quad\; O \end{array} + HCl \qquad (3)$$

This scheme is reproduced in many reviews and books concerning the chemistry of organophosphorus compounds [3]. Evidence in its favor is to be found in the isolation of several cyclic acid chlorides, formed in the second stage, in a pure form [4].

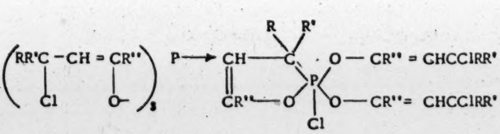
It was suggested by one of us [1] that Conant's scheme is incorrect. This supposition was based on the improbability of such direct alkylation of the phosphorus of phosphorous trichloride, which is so difficult to alkylate, even with alkyl halides.

An alternative to Conant's scheme was suggested in which there occurs 1,4-addition of Cl and the PCl_2 group with formation of a γ-halo unsaturated ester of phosphorous acid:

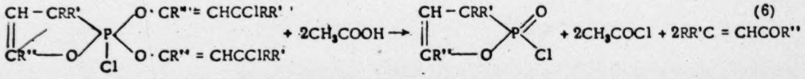

(4)

$$3RR'C=CHCOR'' + PCl_3 \longrightarrow (\begin{array}{l} RR'C-CH=C-R'' \\ \quad\;\; | \qquad\qquad\; | \\ \quad\; Cl \qquad\quad\;\; O- \end{array})_3P \qquad (4)$$

which undergoes the first stage of the A.E.Arbuzov rearrangement:


(5)

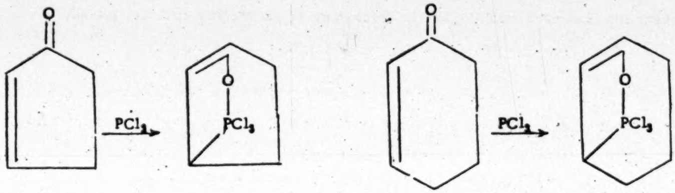
This intermediate product then undergoes acetolysis:


(6)

with formation of a cyclic acid chloride, identical with that assumed in Conant's scheme. The further hydrolysis of the acid chloride leads to a γ-oxoalkylphosphonic acid, in accordance with Equation 3. The regenerated unsaturated ketone again reacts with PCl_3, etc.

We pointed out also that formation of the cyclic acid chloride is not bound to be a stage in the course of this reaction, for the alkylation of a phosphorous ester [5] is not bound to proceed intramolecularly, but may proceed also intermolecularly. Similar phenomena were observed by Kabachnik and Rossiyskaya in a study of the reaction between phosphorus trichloride and ethylene oxide [5], and by Kabachnik and Shepeleva in the reaction between saturated aldehydes and phosphorus trichloride [6]. The scheme we have proposed is in accord with the results of the investigations cited. Nevertheless, it would be impossible to make a choice between the suggested schemes on the basis of the experimental material available in the literature.

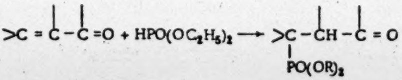
We decided to verify Conant's scheme in the following manner. If the reaction between unsaturated ketones and phosphorus trichloride proceeds by Conant's scheme, then when the reaction occurs with unsaturated cyclic ketones having five- or six-membered rings the following intermediate addition products ought to be formed:



However, molecules of such a structure cannot be formed, for they are bound to be extremely strained: they will contain a multiple bond at the carbon atom that is at the base of the bridge of the bicyclic system. Hence, according to Conant's scheme, unsaturated cyclic ketones cannot add phosphorus trichloride, and therefore the reaction cannot go at all. If, however, phosphorus trichloride does add to unsaturated cyclic ketones with formation after hydrolysis of cyclic γ-oxo acids, then it is clear that the addition reaction proceeds by some other scheme, distinct from that of Conant — probably in accordance with ours.

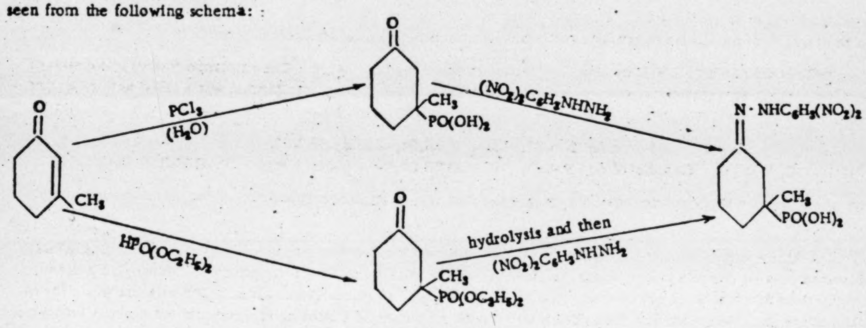
We have carried out the reactions between phosphorus trichloride and two α,β-unsaturated cyclic ketones: 3-methyl-2-cyclohexen-1-one [8] and 2,4-dimethyl-2-cyclopenten-1-one [7]. Phosphorus trichloride readily adds to each of these ketones in acetic acid solution, and the reaction products yield on hydrolysis the corresponding oxocycloalkylphosphonic acids, which we did not succeed in preparing in crystalline form, since they form syrups; they yield, however, 2,4-dinitrophenylhydrazones and p-toluidine salts that crystallize well. From 3-methyl-2-cyclohexen-1-one we obtained the 2,4-dinitrophenylhydrazone of the oxophosphonic acid, m.p. 197°, and from 2,4-dimethyl-2-cyclopenten-1-one we obtained a 2,4-dinitrophenylhydrazone, m.p. 188°, and a p-toluidine salt, m.p. 153-154°.

In order to prove the structure of the keto acids obtained, and of their derivatives, we made use of the recently described reaction of Pudovik and B.A. Arbuzov [9], in which diethylphosphorous acid (diethyl phosphonate) is added to α,β-unsaturated ketones in presence of metallic sodium. This reaction resembles the well known addition reaction of malonic ester at the double bond of an α,β-unsaturated ketone, and there is no doubt that the phosphonic residue adds at the third carbon atom:

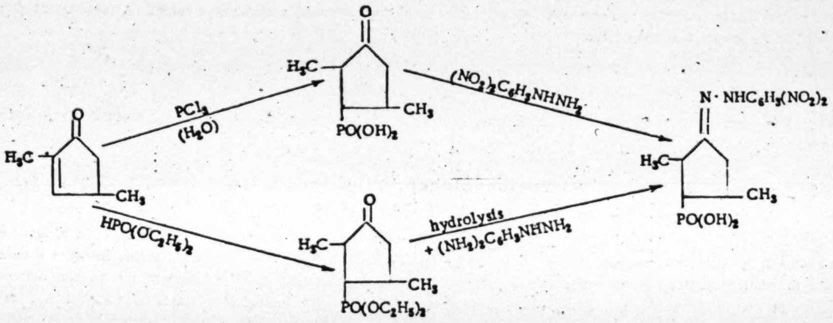


$$>C=\overset{|}{C}-\overset{|}{C}=O + HPO(OC_2H_5)_2 \longrightarrow >\underset{\substack{| \\ PO(OR)_2}}{C}-\overset{|}{C}H-\overset{|}{C}=O$$

On the addition of diethylphosphorous acid to our unsaturated cyclic ketones the formation must occur of the same cyclic γ-oxophosphonic acids must occur as are obtained by the addition of phosphorus trichloride, as will be seen from the following schema: :



PCl₃
(H₂O)
CH₃
PO(OH)₂
(NO₂)₂C₆H₃NHNH₂
N · NHC₆H₃(NO₂)₂
CH₃
PO(OH)₂
HPO(OC₂H₅)₂
hydrolysis and then
(NO₂)₂C₆H₃NHNH₂
CH₃
PO(OC₂H₅)₂



H₃C
CH₃
PCl₃
(H₂O)
H₃C
CH₃
PO(OH)₂
(NO₂)₂C₆H₃NHNH₂
N · NHC₆H₃(NO₂)₂
H₃C
CH₃
PO(OH)₂
HPO(OC₂H₅)₂
H₃C
CH₃
PO(OC₂H₅)₂
hydrolysis
+ (NH₂)₂C₆H₃NHNH₂

Diethylphosphorous acid added readily to each of the unsaturated cyclic ketones with formation of esters of cyclic γ-oxophosphonic acids, which were readily distilled under reduced pressure and were therefore readily purified. When these esters were hydrolyzed by means of hydrochloric acid (1:1), siruplike oxophosphonic acids were formed which, like those obtained by the first method, gave well-crystallizing 2,4-dinitrophenylhydrazones of m.p. 195 and 186° respectively; mixed tests of the hydrazones obtained by the two methods showed no depression in the m.p.; their identity was confirmed also by examination in the polarization microscope: the crystals obtained from the ketone having a six-membered ring (m.p. 195° and 197°) are rhombic in form with an apex angle of 78° and with direct extinction along the diagonal of the rhombus; the crystals obtained from the ketone having a five-membered ring (m.p. 188° and 186°) have the form of very small, fine needles having direct extinction along the axis and perpendicular to the axis.

Thus, it has been proved that addition of phosphorus trichloride to α,β-unsaturated cyclic ketones leads to the corresponding γ-oxophosphonic acids and cannot therefore proceed according to Conant's schema.

EXPERIMENTAL

Preparation of 2,5-Dimethyl-3-oxocyclopentylphosphonic Acid from 2,4-Dimethyl-2-cyclopenten-1-one and Phosphorus Trichloride

Phosphorus trichloride (6.9 g) was added gradually to a mixture of 2,4-dimethyl-2-cyclopenten-1-one (b.p. 82-84° at 47 mm; n_D^{20} 1.4647). (5.5 g) and glacial acetic acid (6 g). The reaction is carried out with cooling; the temperature of the reaction mixture did not exceed + 15° – + 20°. The reaction mixture was left overnight and was then carefully poured into ice water. The water and acetic acid were driven off under reduced pressure, and the residue, a thick dark-colored mass, was dried in a vacuum desiccator over calcium chloride. A syrup (10 g), readily soluble in alcohol but of poor solubility in ether, was obtained. It was not found possible to purify the substance by recrystallization or reprecipitation. On addition to the alcoholic solution of the substance of a solution of p-toluidine in ether, or of an alcoholic solution of aniline, a voluminous white precipitate is formed.

p-Toluidine Salt of 2,5-Dimethyl-3-oxocyclopentylphosphonic Acid. The substance (0.6 g) was dissolved in alcohol, and an ethereal solution of p-toluidine was added. The precipitate formed was washed with ether and dried in a desiccator (0.74 g, m.p. 153-154°).

Found %: N 4.27; 4.35; C 56.74; 56.76; H 7.55; 7.72; P 10.64; 10.06
$C_{14}H_{22}O_4NP$. Calculated %: N 4.67; C 56.20; H 7.36; P 10.35

When attempts were made to recrystallize the p-toluidine salt, partial decomposition of the salt occurred and the m.p. was reduced.

2,4-Dinitrophenylhydrazone of 2,5-Dimethyl-3-oxocyclopentylphosphonic Acid. The substance (2.0 g) was dissolved in ethanol (80 ml) and a freshly prepared alcoholic solution of 2,4-dinitrophenylhydrazine (1.6 g 2,4-dinitrophenylhydrazine, 8 ml sulfuric acid, 12 ml water, and 40 ml alcohol) was added. The mixture was allowed to stand overnight. Next morning the solution was cooled by means of a cooling mixture and the crystals that were precipitated were filtered off and dried in a desiccator over calcium chloride. After recrystallization from 96% ethanol, the hydrazone melted at 188°. The yield was 2.5 g. Calculated on the total reaction mixture (10 g) the yield of the dinitrophenylhydrazone was 66% on the basis of the phosphorus trichloride taken. A preparation dried at 100° in a vacuum was analyzed:

Found %: N 14.70; 14.90; P 8.60; 8.80
$C_{13}H_{17}PN_4O_7$. Calculated %: N 15.0; P 8.33

Very small fine needles; in the polarization microscope they show direct extinction along the axis and normal to the axis.

Preparation of 2,5-Dimethyl-3-oxocyclopentylphosphonic Acid from Diethylphosphorous Acid and 2,4-Dimethyl-2-cyclopenten-1-one

a) Ethyl Ester of 2,5-Dimethyl-3-oxocyclopentylphosphonic Acid. Diethylphosphorous acid (14 g) was added gradually to 2,4-dimethyl-2-cyclopenten-1-one (11 g). A few drops of a solution of sodium ethoxide were then added to the reaction mixture, and the temperature of the reaction mixture rose to 55°. The reaction mixture was cooled with water. When the self-heating had ceased, the reaction mixture was heated on a water bath for 3 hours. It was then vacuum-distilled. As a result of three distillations there was separated a fraction having a b.p. of 119-120° at 3 mm (5.1 g, 20%) of theoretical); n_D^{20} 1.4553; d_4^{20} 1.1022; calculated MR_D 61.87; found MR_D 61.10.

Found %: C 53.19; 53.32; H 8.31; 8.43; P 12.12; 12.10.
$C_{11}H_{21}O_4P$. Calculated %: C 53.23; H 8.47; P 12.50

b) 2,5-Dimethyl-3-oxocyclopentylphosphonic Acid. The ethyl ether of dimethyloxocyclopentylphosphonic acid (2.5 g) and hydrochloric acid (1:1) (75 ml) were boiled under reflux for 15 hours. The solution was then evaporated down on the water-bath, and the residue, a dark-yellow viscous liquid, was dried in a vacuum desiccator over calcium chloride for several days until constant weight was attained. A syrup was obtained.

2,4-Dinitrophenylhydrazone. This was obtained as for the previous hydrazone from 1 g of the syrup and 0.8 g of 2,4-dinitrophenylhydrazine. After two crystallizations from ethanol, bright-yellow crystals (0.9 g, m.p. 186°) were obtained. In admixture with the 2,4-dinitrophenylhydrazone of 2,5-dimethyl-3-oxocyclopentylphosphonic acid obtained by the PCl_3 reaction, it melted at 188°. On examination of the two preparations under the polarization microscope, they appeared to be completely identical.

Preparation of 1-Methyl-3-oxocyclohexylphosphonic Acid from 3-Methyl-2-cyclohexen-1-one and Phosphorus Trichloride.

Freshly distilled phosphorus trichloride (6.9 g) was added to 3-methyl-2-cyclohexen-1-one (b.p. 201-203°; n_D^{20} 1.4926) (5.5 g); the mixture became yellow and its temperature rose to 25°. After 1½ hours, glacial acetic acid (9 g) was added to the mixture; the temperature again rose to 23-25°. The mixture was allowed to stand until the next day, when it was carefully poured into ice water. The water and acetic acid were driven off under reduced pressure, and the residue, a thick brown liquid, was dried in a desiccator over calcium chloride. The syrup did not crystallize after long standing in the desiccator. Yield 9.8 g; it was of good solubility in water and in alcohol, poorly soluble in ether, and insoluble in chloroform. The acid obtained was impure and contained phosphoric acid contamination. The p-toluidine salt has m.p. 147°, the aniline salt m.p. 152°.

2,4-Dinitrophenylhydrazone. The substance (5 g) was dissolved in ethanol (200 ml), and a freshly prepared alcoholic solution of 2,4-dinitrophenylhydrazine (4 g 2,4-dinitrophenylhydrazine, 20 ml sulfuric acid, 30 ml water, and 100 ml ethanol) was added. The mixture was allowed to stand overnight. On the next morning the solution was cooled by means of a cooling mixture, and the crystals that were precipitated were filtered off and dried in a desiccator over calcium chloride. M.p. after recrystallization from ethanol: 197°. The substance crystallizes with one molecule of alcohol; 6.2 g was obtained. The 2,4-dinitrophenylhydrazone forms rhombic crystals having an apex angle of 78°. Under crossed nicols there is direct extinction along the diagonal of the rhombus.

Found %: C 42.55; 42.90; H 5.67; 5.67; N 13.85; 13.90;
P 7.14; 7.15; C_2H_5OH (in a vacuum at 100°) 10.5%.
$C_{13}H_{17}PN_4O_7C_2H_5OH$. Calculated %: C 43.06, H 5.50; N 13.40;
P 7.42, C_2H_5OH 11.0

After being vacuum-dried, the substance melts at 195°.

Found %: P 8.70.
$C_{12}H_{17}PN_4O_7$. Calculated %: P 8.30.

Preparation of 1-Methyl-3-oxocyclohexylphosphonic Acid from Diethylphosphorous Acid and 3-Methyl-2-cyclohexen-1-one

a) Ethyl Ester of 1-Methyl-3-oxocyclohexylphosphonic Acid. Diethylphosphorous acid (14 g) was added to methylcyclohexenone (b.p. 86-89° at 12 mm; n_D^{20} 1.4927) (11 g), and a few drops of a solution of sodium ethoxide were then added to the reaction mixture; the temperature of the reaction mixture rose to 72°. The reaction mixture was heated further for 3 hours on a boiling water-bath, and was then vacuum-distilled. After redistilling, a substance was isolated of b.p. 120-124° at 2 mm (10 g; 40%), colorless liquid; d_4^{20} 1.1188; n_D^{20} 1.4638; found MR_D 61.14, calculated MR_D 61.67.

Found %: C 53.40; 53.30; H 8.39; 8.39; P 12.40; 12.10
$C_{11}H_{21}O_4P$. Calculated %: C 53.23; H 8.47; P 12.50

b) Methyl Ester of 1-Methyl-3-oxocyclohexylphosphonic Acid. Dimethylphosphorous acid (b.p. 72-73° at 10 mm; n_D^{20} 1.4923) (11 g) was added to methylcyclohexenone (b.p. 33° at 3 mm; n_D^{20} 1.3991) (11 g), and a few drops of sodium methoxide solution were then added to the reaction mixture, when the temperature rose to 55°. The reaction mixture was heated further for 3 hours on the water-bath, and on the next day it was vacuum-distilled. After two distillations the fraction of b.p. 127-129° at 2mm was separated, and this crystallized out. The substance obtained melted at 48°.

Found %: C 48.70; 48.70; H 7.40; 7.60; P 13.90; 14.00
$C_9H_{17}PO_4$. Calculated %: C 49.10; H 7.70; P 14.10

c) 1-Methyl-3-oxocyclohexylphosphonic Acid. The ethyl ester of methyloxocyclohexylphosphonic acid (b.p. 124-127° at 2 mm; n_D^{20} 1.4642) (2.5 g) and hydrochloric acid (30 ml, 1:1) were heated in a sealed tube at 130-135° for 2 hours. The contents of the tube were then evaporated down on the water-bath to constant weight. The residual thick dark-yellow liquid was dried in a vacuum desiccator over phosphorus pentoxide to constant weight (several days). The result was a non-crystallizing syrup.

2,4-Dinitrophenylhydrazone. The substance (1.9 g) was dissolved in alcohol (75 ml), and a freshly prepared solution of 2,4-dinitrophenylhydrazine (1.5 g 2,4-dinitrophenylhydrazine, 7.5 ml sulfuric acid, 11.2 ml water, and 37 ml alcohol) was added. The mixture was left overnight, and the crystals that separated were filtered off. After recrystallization from ethanol, bright-yellow glistening crystals were obtained (1 g, m.p. 195°). M.p. in admixture with the 2,4-dinitrophenylhydrazone of m.p. 197° obtained from methylcyclohexenone and phosphorus trichloride was 197°. The two preparations appeared to be identical under the polarization microscope.

SUMMARY

1. Phosphorus trichloride adds to α,β-unsaturated cyclic ketones with formation after hydrolysis of cyclic γ-oxophosphonic acids.

2. Cyclic γ-oxophosphonic acids of identical structure are obtained by the addition of diethylphosphorous acid to α,β-unsaturated cyclic ketones and the subsequent hydrolysis of the esters formed.

3. The fact that cyclic γ-oxophosphonic acids are formed from α,β-unsaturated cyclic ketones disproves Conant's hypothesis concerning the mechanism of the addition of phosphorus trichloride to α,β-unsaturated ketones.

Institute of Organic Chemistry of the USSR Academy of Sciences Received January 28, 1952

LITERATURE CITED

[1] M.I.Kabachnik. Prog. Chem., 16, No. 4, 403 (1947).

[2] J.B.Conant and A.A.Cook. J. Am. Chem. Soc., 42, 830 (1920).

[3] V.M.Plets. Organic Compounds of Phosphorus, Moscow (1939); G.M.Kosolapoff. Organophosphorus Compounds, New York,(1950).

[4] L. Anschutz, E. Klein, and G. Cermak. Ber., 77b, 726 (1944).

[5] M.I.Kabachnik and P.A.Rossiyskaya. Bull. Acad. Sci. USSR, Div. Chem. Sci., 515 (1946).

[6] M.I.Kabachnik and E. S. Shepeleva. Bull.Acad.Sci.USSR, Div.Chem.Sci., 185 (1951).

[7] I.N.Nazarov and L.I.Zaretskaya. Bull.Acad.Sci.USSR, Div.Chem.Sci., 211 (1941); 65 (1944).

[8] E. Knoewenagel and A. Klages. Ann., 281, 94 (1894).

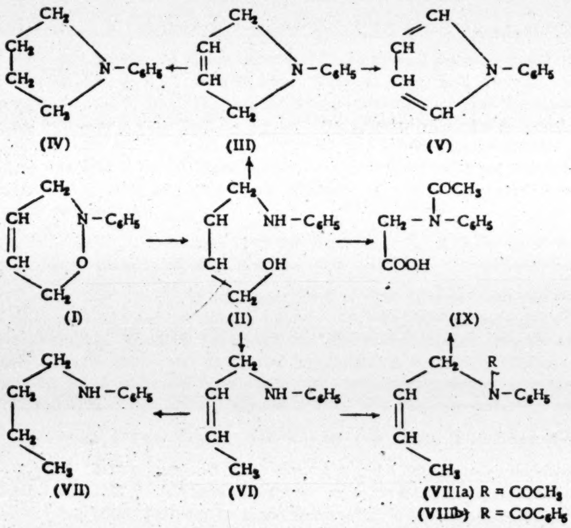
[9] A.N.Pudovik and B.A.Arbuzov. Bull.Acad.Sci.USSR, Div.Chem.Sci., 522 (1949); J.Gen.Chem., 21, 382 (1951) (see Consultants Bureau translation, p.423); Bull. Kazan. Affil. Inst. Acad. Sci. USSR, Chem.Series, No. 1, 53 (1950).

THE REACTIONS OF DIENIC HYDROCARBONS WITH NITROSO COMPOUNDS. ADDITION OF 1,3-BUTADIENE TO NITROSOBENZENE. COMMUNICATION 2.

Yu. A. Arbuzov

It was shown in the previous communication [1] that 1,3-butadiene adds on to nitrosobenzene in accordance with the diene synthesis with formation of 3,6-dihydro-2-phenyl-1,2,2H-oxazine. In this paper, results of experiments on the reduction of this phenyldihydroxazine are given.

It was previously found that reduction of 3,6-dihydro-2-phenyl-1,2,2H-oxazine (I) with zinc dust and acetic acid leads to formation of 4-phenylamino-2-buten-1-ol (II). If, after reducing (I) in this way, the reaction mixture is heated for several hours, then the main reaction product is a crystalline tertiary amine, m.p. 101-102°. Elementary analysis showed that the amine had the composition $C_{10}H_{11}N$. The same amine was obtained by heating 4-phenylamino-2-buten-1-ol (II) with a solution of zinc chloride in acetic or hydrochloric acid, or with a mixture containing acetic, phosphoric, and hydrobromic acids and a small amount of phosphoric anhydride.



It was considered that the tertiary amine, m.p. 101-102°, was 1-phenyl-3-pyrroline (III), formed by the splitting of water from 4-phenylamino-2-buten-1-ol (II). This supposition has been confirmed. Catalytic reduction of the amine gives 1-phenylpyrrolidine (IV), which was identified in the form of its picrate. Oxidation of the amine with potassium permanganate or ferric chloride gives 1-phenylpyrrole (V).

Thus, by means of the reactions indicated we have succeeded in converting a dihydro-o-oxazine ring into a pyrroline ring. (See above).

Different results were obtained when the reduction of 3,6-dihydro-2-phenyl-1,2,2H-oxazine (I) was carried out with sodium and methyl, ethyl, or butyl alcohol. In all these experiments, the main reaction product was a secondary amine (b.p. 89-90° at 3 mm) of composition $C_{10}H_{13}N$. The amine was characterized by means of its acetyl derivative (b.p. 108-109° at 2 mm) and its benzoyl derivative (m.p. 90-91°).

It was considered that the secondary amine of b.p. 89-90° at 3 mm was N-2-butenylaniline (VI), formed from (I) via (II) by further reduction. This supposition was confirmed. Catalytic reduction of the amine gives N-butylaniline (VII), identified as its benzoyl derivative. On oxidation of the acetyl derivative of the amine (VIIIa) with potassium permanganate in acetone, N-acetyl-N-phenylglycine (IX) is formed. Hydrolysis of the acetyl or benzoyl derivative of the amine (VIIIa or VIIIb) with conc. hydrochloric acid yields a crystalline hydroxy amine (m.p. 60.5-61.5°) of composition $C_{10}H_{15}ON$. This hydroxy amine, which is the product formed by addition of the elements of water at the double bond of N-2-butenylaniline (VI), has been prepared previously by Yu. A. Arbuzov and Garburg [2] by hydrolysis with conc. hydrochloric acid of the benzoyl derivative of N-2-butenylaniline, prepared by the reduction of 1-phenylpyrrole with zinc dust and acid.

When 4-phenylamino-2-buten-1-ol (II) is reduced with sodium and ethanol under the same conditions as those employed for the reduction of 3,6-dihydro-2-phenyl-1,2,2H-oxazine (I), N-2-butenylaniline (VI) is formed. In a further experiment, 3,6-dihydro-2-phenyl-1,2,2H-oxazine (I) was reduced by sodium and ethanol to 4-phenylamino-2-buten-1-ol (II), the amount of sodium taken being one-quarter of the amount used in the previous experiments. N-2-Butenylaniline (VI) and 4-phenylamino-2-buten-1-ol (II) were isolated from the products of reaction. The latter could not be separated in the pure state and was converted, for identification, into its dibenzoyl derivative, which melted at 88-89°. The m.p. of a mixture with the pure dibenzoyl derivative of 4-phenylamino-2-buten-1-ol (m.p. 90-91°) was 88-89°. From the above results it follows that, on reduction with sodium and alcohol, 3,6-dihydro-2-phenyl-1,2,2H-oxazine (I) gives 4-phenylamino-2-buten-1-ol (II), which is then reduced further to N-2-butenylaniline (VI).

EXPERIMENTAL

Conversion of 3,6-Dihydro-2-phenyl-1,2,2H-oxazine into 1-Phenyl-3-pyrroline

Expt. 1. Zinc dust (25 g) was introduced into a 250-ml round-bottomed flask containing 3,6-dihydro-2-phenyl-1,2,2H-oxazine (8.06 g; 0.05 mole) dissolved in glacial acetic acid (90 ml). The flask was stoppered and then shaken vigorously for 15 min. The reaction mixture became very hot. The flask was then fitted with a reflux condenser and heated on a water bath for 7 hours. The reaction mixture was cooled, diluted with water (250 ml), and made alkaline with potassium carbonate. The mixture was then steam-distilled. An almost colorless crystalline substance came over in the distillate, and this was filtered off and dried in a desiccator over sulfuric acid. 1-Phenyl-3-pyrroline (3.3 g; 45%), m.p. 95-98°, was obtained. M.p. after two recrystallizations from methanol: 101-102°. Colorless glistening plates.

Found %: C 82.69; 82.71; H 7.58; 7.55; N 9.69; 9.56.
$C_{10}H_{11}N$. Calculated %: C 82.71; H 7.64; N 9.65

Expt. 2. Zinc dust (25 g) was introduced into a 250-ml round-bottomed flask fitted with a reflux condenser with a wide inner tube and containing a solution of 3,6-dihydro-2-phenyl-1,2,2H-oxazine (16.1g 0.1 mole) in glacial acetic acid (50 ml). The flask was shaken, and the reaction mixture grew hot and finally boiled vigorously for several minutes. The mixture was then boiled for 4 hours. It was cooled, diluted with 100 ml of water, and rendered alkaline with a 40% solution of caustic soda. The 1-phenyl-3-pyrroline was steam-distilled off, filtered off, and dried (11.2 g; 77% of theoretical. M.p. 94.5-98°). M.p. after two recrystallizations from methanol: 101-102°.

Conversion of 4-Phenylamino-2-buten-1-ol into 1-Phenyl-3-pyrroline

Expt. 1. 4-Phenylamino-2-buten-1-ol (16.3 g, 0.1 mole) and a solution of anhydrous zinc chloride (10 g) in glacial acetic acid (50 ml) were introduced into a 100-ml round-bottomed flask fitted with a reflux condenser. The mixture was boiled for 4 hours. It was then cooled, and additions were made of 100 ml water and 100 g caustic soda. The 1-phenyl-3-pyrroline was steam-distilled off, filtered off, and dried (10.6 g; 73% of theoretical). M.p. after two recrystallizations from methanol: 100.5-101.5°.

Expt. 2. 4-Phenylamino-2-buten-1-ol (32.6 g, 0.2 mole) and 40 g of zinc chloride solution in conc. HCl (160 ml) were introduced into a 250-ml round-bottomed flask fitted with a reflux condenser. The mixture was boiled for 4 hours and then cooled. A 40% solution of caustic soda was added until the reaction was alkaline, and the 1-phenyl-3-pyrroline was steam-distilled off. The yield was 21.2 g (73% of theoretical). M.p. after recrystallization from methanol was 100-101°.

Expt. 3. 4-Phenylamino-2-buten-1-ol (32.6 g, 0.2 mole), 100 ml of glacial acetic acid, and 20 ml of 85% phosphoric acid were introduced into a 250-ml round-bottomed flask fitted with a reflux condenser. The mixture was boiled for 5 hours, cooled, and rendered alkaline with a 40% solution of caustic soda. The 1-phenyl-3-pyrroline was steam-distilled off (15.6 g, 54% of theoretical). M.p. after recrystallization from methanol was 100-101°.

Expt. 4. 4-Phenylamino-2-buten-1-ol (16.3 g, 0.1 mole) and 50 ml of 40% hydrobromic acid were introduced into a 100-ml flask fitted with a reflux condenser. The mixture was boiled for 4 hours, cooled, and rendered alkaline with 40% caustic soda solution. The 1-phenyl-3-pyrroline was steam-distilled off (12.0 g, 83% of theoretical).

Expt. 5. 4-Phenylamino-2-buten-1-ol (32.6 g, 0.2 mole) and 1 g of phosphoric anhydride were introduced into a 100-ml distillation flask fitted with thermometer and air condenser arranged for distillation. The flask was heated on a metal bath. At first a small amount of water came over, and then, at 245-250°, 1-phenyl-3-pyrroline came over. The yield after steam-distillation was 24.1 g (83% of theoretical). M.p. after recrystallization from methanol was 99.5-101°.

Catalytic Reduction of 1-Phenyl-3-pyrroline into 1-Phenylpyrrolidine

1-Phenyl-3-pyrroline (7.25 g, 0.05 mole) was dissolved in 120 ml cyclohexane and reduced in presence of platinized (10% Pt) charcoal (1 g) at room temperature and pressure. Reduction was complete in 4 hours. Volume of hydrogen absorbed: 1330 ml (0° at 760 mm). The catalyst was filtered off, the cyclohexane was driven off, and the residue was vacuum-distilled. The product was 1-phenylpyrrolidine (6.0 g, 82% of theoretical) with the following constants: b.p. 102-103° at 5 mm; d_4^{20} 1.0157; n_D^{20} 1.5827; found MR_D 48.42; calculated MR_D 46.52;) EMR_D 1.90. Calculated 82% of theoretical. It solidified to a crystalline mass on being cooled with tap water.

Data in the literature [3]: b.p. 124° at 14 mm; [4] b.p. 110-116° at 9 mm; d^{25} 1.026; n_D^{25} 1.5803; [5] b.p. 114° at 9 mm; d_4^{20} 1.0183; n_D^{20} 1.5853; [2] b.p. 129-130° at 16 mm; d_4^{20} 1.0145; n_D^{20} 1.5820.

Found %: C 81.68, 81.43; H 8.67, 8.78; N 9.56, 9.47
$C_{10}H_{13}N$. Calculated %: C 81.59 H 8.90 N 9.51

1-Phenylpyrrolidine Picrate. A warm ethereal solution of picric acid (2.3 g, 0.01 mole) was mixed with an ethereal solution of 1.5 g, (0.01 mole) of 1-phenylpyrrolidine. Next day the picrate was filtered off and washed with ether (3.6 g, m.p. 114-115°). M.p. after recrystallization from ethanol was 116-117°. Data in the literature: [3] m.p. 114°; [4] m.p. 115-116°;) [5] m.p. 116°; [2] m.p. 116-117°.

For comparison, 1-phenylpyrrolidine and its picrate were prepared. The phenylpyrrolidine was obtained as follows: 1,4-dibromobutane (108 g, 0.5 mole) and freshly distilled aniline (140 g, 1.5 mole) were introduced into a 500-ml round-bottomed flask fitted with a reflux condenser. The mixture was heated on a boiling water-bath for 4 hours and then cooled. A 40% solution of caustic soda was added until the precipitate had completely dissolved. The oil that formed was separated, washed with 10% caustic soda solution and with water, dried with fused caustic soda, and vacuum-fractionated. The product was 1-phenylpyrrolidine (62.5 g, 85% of theoretical) with the following constants: b.p. 103-103.5° at 5 mm; d_4^{20} 1.0162; n_D^{20} 1.5829; found MR_D 48.40; calculated MR_D 46.52; EMR_D 1.88.. The picrate obtained from this preparation had a m.p. of 116-117° after recrystallization from ethanol. In admixture with the picrate of 1-phenylpyrrolidine obtained from 1-phenyl-3-pyrroline, it melted at the same temperature.

Oxidation of 1-Phenyl-3-pyrroline to 1-Phenylpyrrole by means of Potassium Permanganate

A solution of potassium permanganate (4.7 g, 0.03 mole) in 300 ml dry acetone was added over 2.5 hours with continuous stirring to a solution of 1-phenyl-3-pyrroline (4.35 g, 0.03 mole) in 300 ml dry acetone. Next day the precipitate was filtered off and the acetone driven off. 50 ml hydrochloric acid (diluted 1:1) was added to the residue, and the mixture was steam-distilled. A colorless crystalline substance went over into the distillate; it was filtered off, washed with water, and dried over sulfuric acid in a desiccator. The product was 1-phenylpyrrole (1.50 g, 35% of theoretical), m.p. 59.5-60.5°. In admixture with 1-phenylpyrrole (m.p. 60-61°) prepared from aniline mucate it melted at 60-61°. Data in the literature: [6] m.p. 62°; [7] m.p. 61.5°; [8] m.p. 60-61°; [9] m.p. 61-62°; [10] m.p. 60-61; [11] m.p. 60-61°; [12] m.p. 58°; [2] m.p. 61-62°.

Oxidation of 1-Phenyl-3-pyrroline to 1-Phenylpyrrole by means of Ferric Chloride

A solution of ferric chloride hexahydrate (10.8 g, 0.04 mole) in 50 ml water was added with stirring to a solution of 1-phenyl-3-pyrroline (2.90 g, 0.02 mole) in 60 ml hydrochloric acid (diluted 1:1). After 1 hour, the 1-phenylpyrrole was steam-distilled off (1.40 g, 49% of theoretical; m.p. 58-59°). In admixture with 1-phenylpyrrole (m.p. 60-61°) prepared from aniline mucate it melted at 60-61°.

Reduction of 3,6-Dihydro-2-phenyl-1,2,2H-oxazine to N-2-Butenylaniline by means of Sodium and Alcohol

Expt. 1. A solution of 3,6-dihydro-2-phenyl-1,2,2H-oxazine (32.2 g, 0.2 mole) in 650 ml absolute ethanol was introduced into a 3-liter round-bottomed flask fitted with a wide branched adapter and with a reflux condenser having a wide inner tube. The solution was heated to boiling, and 50 g sodium (about 2.2 g-atom) was introduced in small portions over 10 minutes. Heating was continued until the sodium had completely dissolved. The [illegible] reaction mixture was cooled, and hydrochloric acid (diluted 1:1) was added until the solution became acid to Congo red. The alcohol was steam-distilled off. Potassium carbonate was added to give an alkaline reaction, and the mixture was steam-distilled. A light-yellow oil came over in the distillate. The oil was separated, and the aqueous layer was extracted three times with ether (3 · 100 ml). The ether extract was united with the oil, and the solution was dried with anhydrous sodium sulfate. The ether was driven off, and the residue was fractionated. N-2-Butenylaniline (19.9 g, 68% of theoretical) was obtained; it had the following constants: b.p. 89-90° at 3 mm; d_4^{20} 0.9613; n_D^{20} 1.5587; found MR_D 49.42; calculated MR_D 47.91; EMR_D 1.51. It is a colorless, fairly mobile liquid that gradually yellows during storage.

Found %: C 81.42, 81.43; H 8.86, 8.84; N 9.66, 9.76
$C_{10}H_{13}N$. Calculated %: C 81.59; H 8.90; N 9.51.

Expt. 2. A solution of 3,6-dihydro-2-phenyl-1,2,2H-oxazine (48.3 g, 0.3 mole) in 1 liter absolute butanol was introduced into a 3-liter round-bottomed flask connected through a branched adapter to a reflux condenser. The solution was heated to boiling, and 75 g sodium (about 3.3 g-atom) was introduced in small portions over 15 minutes. Heating was continued until the sodium had completely dissolved. Further treatment was carried out as in Expt. 1. N-2-Butenylaniline (28.5 g, 65% of theoretical was obtained, with the following constants: b.p. 93-94° at 4.5 mm; d_4^{20} 0.9609; n_D^{21} 1.5587; found MR_D 49.44; calculated MR_D 47.91; EMR_D 1.53.

Expt. 3. A solution of 3,6-dihydro-2-phenyl-1,2,2H-oxazine (32.2 g, 0.2 mole) in 500 ml absolute ethanol was introduced into a 3-liter round-bottomed flask connected through a branched adapter to a reflux condenser. The solution was heated to boiling, and 50 g sodium (about 2.2 g-atom) was introduced in small portions over 10 minutes. Heating was continued until the sodium had completely dissolved. The further treatment was as in the preceding experiments. N-2-Butenylaniline (12.0 g, 41% of theoretical) was obtained, with the following constants: b.p. 89-90° at 3 mm; d_4^{20} 0.9620; n_D^{19} 1.5590; found MR_D 49.40;) calculated MR_D 47.91; EMR_D 1.49.

Reduction of 4-Phenylamino-2-buten-1-ol to N-2-Butenylaniline by means of Sodium and Alcohol.

A solution of 4-phenylamino-2-buten-1-ol (16.3 g, 0.1 mole) in 350 ml absolute ethanol was introduced into a 2-liter round-bottomed flask connected through a branched adapter to a reflux condenser. The solution was heated to boiling, and 25 g sodium (about 1.1 g-atom) was introduced in small portions over 8 minutes. Heating was continued until the sodium had completely dissolved. The mixture was then cooled and acidified with diluted HCl. The alcohol was steam-distilled off, and the residue was rendered alkaline with potassium carbonate. N-2-Butenylaniline was steam-distilled over (9.9 g, 67% of theoretical), with the following constants: b.p. 87-88° at 2 mm; d_4^{20} 0.9611; n_D^{20} 1.5586; found MR_D 49.42; calculated MR_D 47.91; EMR_D 1.51.

Reduction of 3,6-Dihydro-2-phenyl-1,2,2H-oxazine to 4-Phenylamino-2-buten-1-ol by means of Sodium and Alcohol

A solution of 3,6-dihydro-2-phenyl-1,2,2H-oxazine (32.2 g, 0.2 mole) in 350 ml absolute ethanol was introduced into a 2-liter round-bottomed flask connected through a branched adapter to a reflux condenser. The solution was heated to boiling, and 12.5 g sodium (about 0.54 g-atom) was introduced in the form of small cubes over 15 minutes. Heating was continued until the sodium had completely dissolved. The mixture was then cooled and acidified with hydrochloric acid. The alcohol was steam-distilled off, and the residue was rendered alkaline with 40% aqueous caustic soda. N-2-Butenylaniline was steam-distilled over (6.3 g), with the following constants: b.p. 90-91° at 3 mm; d_4^{20} 0.9628; n_D^{20} 1.5594; found MR_D 49.39; calculated MR_D 47.91; EMR_D 1.48.

The mixture that remained after distilling off the N-2-butenylaniline in steam was cooled and extracted 5 times with benzene (5 · 100 ml). The benzene solution was washed with water, the benzene was driven off, and the residue was vacuum-fractionated. A fraction (12.3 g) was collected with the following constants: b.p. 148-152° at 2 mm; d_4^{26} 1.1193; n_D^{23} 1.5866.

Benzoylation of the Fraction having a B.P. of 149-152° at 2 mm

Some of the fraction (4.90 g) and 60 ml of 10% aqueous caustic soda were introduced into a flask, and 14.1 g of benzoyl chloride was added in 5 portions over 30 minutes with energetic shaking. The excess benzoyl chloride was hydrolyzed by warming. The product of benzoylation was filtered off, washed with water, and recrystallized from ethanol. The product was the dibenzoyl derivative of 4-phenylamino-2-buten-1-ol (9.0 g), m.p. 87-88.5°. M.p. after repeated recrystallization from ethanol was 88-89°.

Found %: N 3.82, 3.94
$C_{24}H_{21}O_3N$. Calculated %: N 3.77

In admixture with the dibenzoyl derivative of 4-phenylamino-2-buten-1-ol obtained by the reduction of 3,6-dihydro-2-phenyl-1,2,2H-oxazine with zinc and acetic acid (m.p. 90-91°) it melted at 88-89°.

Catalytic Reduction of N-2-Butenylaniline to N-Butylaniline

N-2-Cutenylaniline (7.36 g, 0.05 mole) was dissolved in 70 ml cyclohexane and reduced in presence of platinized (10% Pt) charcoal (1 g) at room temperature and pressure. Reaction was complete in 60 minutes. Volume of hydrogen absorbed: 1500 ml (0°, 760 mm). The catalyst was filtered off, the cyclohexane was driven off, and the residue was fractionated. N-Butylaniline (6.0 g, 80% of theoretical) was obtained; it had the following constants: b.p. 97-98° at 5 mm; d_4^{20} 0.9338; n_D^{20} 1.5361; found MR_D 49.83; calculated MR_D 48.38; EMR_D 1.45 rature: Data in the literature: [14]; b.p. 119-120° at 12 mm; [15]: b.p. 118-120° at 14 mm; [16]: b.p. 115-120° at 15 mm; ; d_4^{20} 0.9358; n_D^{20} 1.5381; b.p. 112-114° at 9 mm; d_4^{20} 0.9362; n_D^{20} 1.5373.

Found %: C 80.45, 80.69; H 10.05, 10.04; N 9.33, 9.10
$C_{10}H_{15}N$. Calculated %: C 80.50; H 10.12; N 9.38

Benzoylation of N-Butylaniline

N-Butylaniline (3.0 g, 0.02 mole) and 20 ml of 10% aqueous caustic soda were introduced into a flask, and 4.2 g (0.03 mole) benzoyl chloride was added in 3 portions over 15 minutes. After each addition of benzoyl chloride, the flask was closed by means of a stopper and shaken vigorously. Excess benzoyl chloride was hydrolyzed by warming on the water-bath. The reaction product was filtered off, washed with water, and dried in a desiccator over sulfuric acid. The product was N-butylbenzanilide (4.9 g, 96% of theoretical), m.p. 47-50°. M.p. after two recrystallizations from petroleum ether was 52.5-53.5°. Data in the literature: [17] b.p. 55°; [18] b.p. 47-48°.

For comparison, N-butylaniline and its benzoyl derivative were prepared. N-Butylaniline prepared from aniline and butyl bromide by Hickenbottom's method [19] had the following constants: b.p. 97-97.5° at 5 mm; d_4^{20} 0.9325; n_D^{20} 1.5350; found MR_D 49.81; calculated MR_D 48.38; EMR_D 1.43. The m.p. of N-butylbenzanilide obtained from this preparation and crystallized from petroleum ether was 53-54°. In admixture with the benzoyl derivative of N-butylaniline obtained from N-2-butenylaniline it melted at 52.5-53.5°.

Acetylation of N-2-Butenylaniline

Expt. 1. N-2-Butenylaniline (14.7 g, 0.1 mole) and 50 ml water were introduced into a flask provided with a mechanical stirrer. The stirrer was switched on, and 11.2 g acetic anhydride (0.11 mole) was added to the aqueous emulsion of amine. Stirring was continued for 30 minutes. Ether was then added, and the upper layer was separated. The aqueous layer was made alkaline with sodium carbonate and extracted with ether. The united ether extracts were washed with 5% sodium carbonate, then with water; they were dried with anhydrous potassium carbonate. The ether was distilled off, and the residue was fractionated. N-2-Butenylacetanilide (VIIIa) (14.1 g, 75% of theoretical) was obtained, with the following constants: b.p. 108-109° at 2 mm; d_4^{20} 1.0137; n_D^{20} 1.5324; found MR_D 57.87; calculated MR_D 57.15; EMR_D 0.72. It is a colorless viscous liquid. Data in the literature [13] b.p. 165-168° at 28 mm.

Found %: C 75.99, 75.74; H 8.09, 7.99; N 7.57, 7.54
$C_{12}H_{15}ON$. Calculated %: C 76.16; H 7.98; N 7.40

Expt. 2. N-2-Butenylaniline (17.7 g, 0.12 mole) dissolved in 40 ml acetic anhydride was introduced into a flask furnished with a reflux condenser. The mixture was heated on a boiling water bath for 3.5 hours. The acetic acid and acetic anhydride were then distilled off under reduced pressure (45 mm), and the residue was distilled at 2 mm. N-2-Butenylacetanilide (VIIIa) (21.2 g, 93% of theoretical) was obtained, with the following constants: b.p. 108-109° at 2 mm; d_4^{20} 1.0144; n_D^{20} 1.5328; found MR_D 57.87; calculated MR_D 57.15; EMR_D 0.72.

Oxidation of N-2-Butenylacetanilide to N-Acetyl-N-phenylglycine

A solution of potassium permanganate (4.7 g, 0.03 mole) in 325 ml dry acetone was added over 2 hours with constant stirring to a solution of N-2-butenylacetanilide (1.89 g, 0.01 mole) in 100 ml dry acetone. On the next day the precipitate was filtered off, washed on the filter with acetone, and extracted with 50 ml water. The aqueous extract was extracted with chloroform and acidified with diluted hydrochloric acid. The precipitate was filtered off, washed with cold water, and dried in a desiccator over sulfuric acid. N-Acetyl-N-phenylglycine (0.77 g, 40% of theoretical), m.p. 189-192°, was obtained. M.p. after recrystallization from hot water was 193.5-195°. In admixture with N-acetyl-N-phenylglycine (m.p. 193-195°) obtained by the acetylation of N-phenylglycine it melted at 193.5-195°.

Hydrolysis of N-2-Butenylacetanilide with Hydrochloric Acid

N-2-Butenylacetanilide (18.9 g, 0.1 mole) and 250 ml conc. HCl were introduced into a flask fitted with a reflux condenser. The mixture was boiled for 6 hours. It was then cooled, diluted with 250 ml water, and rendered alkaline with 40% aqueous caustic soda. The oil that separated was extracted with ether, and the ethereal solution was washed with water and then dried with anhydrous sodium sulfate. The ether was driven off, and the residue was vacuum-distilled. A fraction (10.9 g) of b.p. 120-125° at 1 mm was obtained. After a short time, this fraction partially crystallized. The crystals were filtered off and washed with absolute ether. The crystals (5.8 g, 35% of theoretical) were almost colorless; m.p. 59-61°. M.p. after recrystallization from cyclohexane was 60.5-61.5°. Data in the literature: [2] m.p. 60.5-61.5°.

Found %: C 72.69, 72.75; H 8.97, 8.99; N 8.47, 8.47

$C_{10}H_{13}ON$. Calculated %: C 72.69; H 9.15; N 8.48

Benzoylation of N-2-Butenylaniline

N-2-Butenylaniline (5.9 g, 0.04 mole) was emulsified in a 10% solution of caustic soda (40 g of solution). Benzoyl chloride (8.4 g, 0.06 mole) was added to the emulsion in 5 portions over 20 minutes with energetic shaking. Excess benzoyl chloride was hydrolyzed by warming on the water bath. The benzoylation product was filtered off, washed with water, and dried in a desiccator over sulfuric acid. N-2-Butenylbenzanilide (VIIIb) (9.6 g, 95% of theoretical) was obtained. M.p. 85-89°; m.p. after two recrystallizations from ethanol was 90-91°. Data in the literature: [18] b.p. 204-207° at 13 mm; [2] m.p. 90-91°.

Found %: C 81.17, 81.14; H 6.89, 6.79; N 5.30, 5.28

$C_{17}H_{17}ON$. Calculated %: C 81.24; H 6.82; N 5.57

Hydrolysis of N-2-Butenylbenzanilide with Hydrochloric Acid

N-2-Butenylbenzanilide (12.6 g, 0.05 mole) and 125 ml conc. HCl were introduced into a flask fitted with a reflux condenser, and the mixture was boiled for 8 hours. It was then cooled, diluted with 125 ml water, and extracted with ether to remove benzoic acid (yield 5.8 g). The acid solution was rendered alkaline with caustic soda, and the oil that separated was dissolved in ether. The ethereal solution was dried with anhydrous sodium sulfate; the ether was driven off, and the residue was vacuum-distilled. A fraction (5.1 g) of b.p. 131-137° at 3 mm was obtained; it partially crystallized out on standing. The crystals were filtered off and washed with absolute ether. The product was the hydroxy amine $C_{10}H_{13}ON$ (2.5 g, 30% of theoretical), m.p. 59-61°. M.p. after recrystallization from cyclohexane was 60.5-61.5°.

In conclusion I express my deep gratitude to A.N.Nesmeyanov for his valuable advice and for his constant interest in my work.

SUMMARY

1. It has been found that when 3,6-dihydro-2-phenyl-1,2,2H-oxazine is reduced by means of zinc dust and acetic acid under severe conditions, 1-phenyl-3-pyrroline is formed.

2. It has been found that when 3,6-dihydro-2-phenyl-1,2,2H-oxazine is reduced by means of sodium and alcohol, N-2-butenylaniline is formed.

3. It has been shown that when 3,6-dihydro-2-phenyl-1,2,2H-oxazine is reduced to give 1-phenyl-3-pyrroline, 4-phenylamino-2-buten-1-ol is formed as an intermediate product.

Institute of Organic Chemistry of the USSR Academy of Sciences

Received January 2, 1952

LITERATURE CITED

[1] Yu.A.Arbuzov. Bull.Acad.Sci.USSR, Div.Chem.Sci., No. 2, 344 (1952).*

[2] Yu.A.Arbuzov and M.M.Garburg. Bull.Acad.Sci.USSR, Div.Chem.Sci., No. 3, 556 (1952).**

[3] J.Braun and G.Lemke. Ber., 55, 3556 (1922).

[4] F.Signaigo and H.Adkins. J.Am.Chem.Soc., 58, 709 (1936).

[5] Yu.K. Yuriev and G.A.Minkina. J.Gen.Chem., 7, 2945 (1937).

[6] M.Köttnitz. J.prak.Chem., [2], 6, 136 (1872).

[7] M. de Jong and J.P.Wibaut. Rec. Trav. Chim., 49, 243 (1930).

[8] L.C.Craig and R.M.Hixon. J.Am.Chem.Soc., 52, 804 (1930).

[9] Yu.K Yuriev. Ber., 69, 1944 (1936); J.Gen.Chem., 7, 267 (1937).

[10] C.F.H.Allen, M.R.Gibbert, and D.M.Young. J.Org.Chem., 2, 227 (1937).

[11] H.Adkins and H.L.Coonradt. J.Am.Chem.Soc., 63, 1556 (1941).

[12] F.Blicke and J.Powers. J.Am.Chem.Soc., 198 (1934).

[13] W.J.Hickinbottom. J.Chem.Soc., 198 (1934).

[14] J.Braun and R Murjahn. Ber., 59, 1202 (1926).

[15] K.H.Slotta and W.Franke. Ber., 63, 678 (1930).

[16] V.C.Sekera and C.S.Marvel. J.Am.Chem.Soc., 55, 345 (1933).

[17] W.H.Mills, J.E.G.Harris, and H.Lambourne. J.Chem.Soc., 119, 1294 (1921).

[18] O.Mumm and F.Möller. Ber.,70, 2214 (1937).

[19] W.J.Hickinbottom. J.Chem.Soc., 992 (1930).

---

* See Consultants Bureau translation, p. 339.

** See Consultants Bureau translation, p. 531.

BLANK
PAGE

REDUCTION OF 1-PHENYLPYRROLE

Yu. A. Arbuzov and M. M. Garburg

Addition of hydrogen to the pyrrole nucleus proceeds in two stages: first, dihydro derivatives are formed, and then tetrahydro derivatives. Reduction of the pyrrole nucleus with addition of two hydrogen atoms and formation of pyrrolines has been described in adequate detail only for pyrrole itself.

The oldest method for the reduction of pyrrole to pyrroline is that of Ciamician [1], which consists in reduction with zinc dust and acetic acid, with application of heat. Knorr and Rabe [2] found that the reduction of pyrrole to pyrroline goes better when zinc dust and hydrochloric acid are used. Zelinsky and Yuryev [3] proposed the use of zinc-palladium and hydrochloric acid for this purpose. Reduction of pyrrole homologs to pyrrolines has been described for 1-methylpyrrole [4], 2,3-dimethylpyrrole [5], 2,4-dimethylpyrrole [2], 2,5-dimethylpyrrole [2,29], and 1,2,5-trimethylpyrrole [2]. On the basis of the propensity shown by compounds having two conjugated double bonds to give 1,4-addition reactions, the dihydro derivatives obtained by the reduction of pyrrole and its homologs were regarded as 2,5-dihydro derivatives (3-pyrrolines). This was shown to be so for pyrroline itself by Treibs and Dinelli [6], who obtained iminodiacetic acid by the ozonolysis of pyrroline.*

Later, several papers were published in which descriptions were given of the reduction by zinc dust and hydrochloric acid of certain C-arylpyrroles to 2-pyrrolines. Thus Sohn [7] found that reduction of 2-methyl-4-phenylpyrrole yields 2-methyl-4-phenyl-2-pyrroline. According to Sohn's results [8], 4-methyl-2-phenylpyrrole also unites with hydrogen in the 4,5-positions with formation of 4-methyl-2-phenyl-2-pyrroline. Sohn gives the conjugation of the double bonds of the benzene and pyrrole nuclei as the explanation of the reduction of C-arylpyrroles to 2-pyrrolines. Wibaut [9], by reducing 2-phenylpyrrole, obtained a dihydro derivative to which he ascribed the structure of 5-phenyl-2-pyrroline. In a further communication [10], Wibaut stated that by the reduction of 2-(p-chlorophenyl)pyrrole, 2-(m-chlorophenyl)pyrrole, 2-(o-chlorophenyl)pyrrole, and 2-(m-bromophenyl)pyrrole, 2,3-dihydro derivatives are again formed. By the reduction of 1-methyl-2-β-pyridyl)pyrrole (nicotyrine) Wibaut [11] obtained dihydronicotyrine, to which Spath and Wibaut [12] ascribed the structure of 1-methyl-2-β-pyridyl-2-pyrroline (N-methylmyosmine). However, in 1950 Haines and Eisner [13] synthesized N-methylmyosmine and found that it is not identical with Wibaut's dihydronicotyrine. In 1951, King [14] found that, on ozonolysis of 2-phenylpyrroline prepared by the reduction of 2-phenylpyrrole with zinc dust and hydrochloric acid, α-phenyl-α,α'-iminodiacetic acid is formed. Hence, it was established that 2-phenylpyrrole unites with hydrogen in the 2,5-positions with formation of 2-phenyl-3-pyrroline. It must be supposed that in the reduction of nicotyrine a 3-pyrroline derivative (1-methyl-2-β-pyridyl-3-pyrroline) is formed.**

From the above it follows that also the remainder of the work cited on the reduction of 2-arylpyrroles to 2-pyrrolines requires critical review. The aim of the present work is to investigate the reduction of 1-phenylpyrrole and to study the possibility of preparing by this means 1-phenyl-3-pyrroline, which was prepared by one of us [15] by the reduction of 3,6-dihydro-2-phenyl-1,2,2H-oxazine (nitrosobenzene adduct of 1,3-butadiene) by means of zinc dust and acetic acid.

1-Phenylpyrrole is generally prepared by thermal decomposition of aniline mucate [16-21]. We obtained 1-phenylpyrrole in 56% yield by the thermal decomposition of aniline mucate in presence of aluminum oxide.*** When the decomposition was carried out in absence of aluminum oxide, the yield of 1-phenylpyrrole was only 42%. For 1-phenylpyrrole, reduction with addition of two hydrogen atoms has not been described. Only its catalytic reduction to 1-phenylpyrrolidine [23] or to 1-cyclohexylpyrrolidine [19,22,23] has been described. In view of the readiness with which hydrogen unites with pyrrole and its homologs, our trials on the reduction of

---

* Evans [28] has found recently that when pyrrole homologs are reduced with zinc dust and hydrochloric acid, a mixture of isomeric pyrrolines is formed. Thus, 2,5-dimethyl-3-pyrroline (about 80%) and 2,5-dimethyl-1-pyrroline (about 20%) were isolated from the reduction products of 2,5-dimethylpyrrole. Reduction of 1,2,5-trimethylpyrrole and of 2-methylpyrrole led also to mixtures of isomeric dihydro derivatives.

** In a recent paper, Wibaut [30] considers that the structure of 1-methyl-2-(β-pyridyl)-3-pyrroline is the most probable one for dihydronicotyrine.

*** Aluminum oxide has been employed by Chichibabin [24] in the preparation of 1-(α-pyridyl)pyrrole from a mixture of α-aminopyridine and mucic acid.

1-phenylpyrrole were made under the mildest conditions possible. Nevertheless, it was found that, when treated with zinc dust and acetic acid, both cold and hot, 1-phenylpyrrole did not unite with hydrogen.

Treatment of 1-phenylpyrrole with zinc dust and hydrochloric acid at 60-75° led to the formation of an oil, which consisted of a mixture of reduction products. Elementary analysis of the main fraction of the reduction product (b.p. 90-92° at 3 mm) showed that under these conditions of reduction four hydrogen atoms add to the 1-phenylpyrrole molecule. Similar results were obtained by the action on 1-phenylpyrrole of zinc dust with hydrochloric and acetic acids at 50-65° and at 40-50°. The mixture of reduction products was subjected to benzoylation, and a liquid tertiary amine and a crystalline benzoylation product were isolated. The constants of the tertiary amine, after purification by vacuum-distillation, showed it to be 1-phenylpyrrolidine. For comparison, some 1-phenylpyrrolidine was synthesized from 1,4-dibromobutane and aniline, and picrates were prepared from both compounds. A mixed m.p. on the picrates showed no depression. Thus, the tertiary amine that we obtained by the reduction of 1-phenylpyrrole was 1-phenylpyrrolidine.

After recrystallization from ethanol, the crystalline benzoylation product melted at 90-91°. Elementary analysis of this substance showed it to have the composition $C_{17}H_{17}ON$. The substance was subjected to hydrolysis by means of hydrochloric acid, and a crystalline product, m.p. 60.5-61.5° was obtained. Elementary analysis of the substance showed it to have the composition $C_{10}H_{15}ON$. Hence, as a result of hydrolysis with hydrochloric acid the substance gave not the expected amine of composition $C_{10}H_{13}N$, but the product formed by addition of a molecule of water to this amine.

Hydrolysis of the crystalline benzoylation product with alcoholic alkali yielded a liquid amine having constants close to those of N-2-butenylaniline, which was obtained by one of us [15] by the reduction of 3,6-dihydro-2-phenyl-1,2,2H-oxazine by means of sodium and alcohol. For comparison, the benzoyl derivative of N-2-butenylaniline was prepared; it melted at 90-91°. A mixture of the two compounds melted without depression. Hence, the crystalline benzoylation product was the benzoyl derivative of N-2-butenylaniline. The formation of a compound of composition $C_{10}H_{15}ON$ by hydrolysis of the benzoyl derivative of N-2-butenylaniline by means of hydrochloric acid may be explained by the occurrence, simultaneously with hydrolysis, of addition of the elements of water at the double bond.*

By the benzoylation of the low-boiling fraction (b.p. up to 92° at 4 mm) obtained by the reduction of 1-phenylpyrrole by means of zinc dust and hydrochloric and acetic acids at 40-50°, benzanilide, m.p. 162-163°, was obtained.

As the above-given results of our experiments show, reduction of 1-phenylpyrrole under the conditions that we have studied leads to the formation of 1-phenylpyrrolidine, N-2-butenylaniline, and aniline. We have found that 1-phenyl-3-pyrroline is not reduced by zinc dust in conjunction with hydrochloric and acetic acids at 40-50°, and this result excludes the possibility of the intermediate formation of 1-phenyl-3-pyrroline as a stage in the reduction of 1-phenylpyrrole. There remains the possibility that the first stage in the reduction of 1-phenylpyrrole is the formation of 1-phenyl-2-pyrroline.

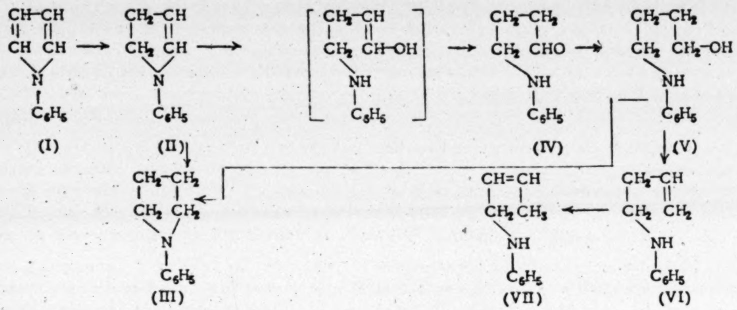
It has been established by the work of Lipp and Markwalder that N-phenyl-2-piperideines and N-phenyl-2-pyrrolines can exist only in the form of salts. Thus, Lipp [26] found that, when aniline reacts with 6-bromo-2-hexanone, the hydrobromide of 1,2,3,4-tetrahydro-6-methyl-1-phenylpyridine is formed. When attempts were made to isolate the free base from the hydrobromide, hydrolytic opening of the piperideine ring occurred, and 6-phenylamino-2-hexanone was formed. When the 6-phenylamino-2-hexanone was treated with acids, the piperideine ring was reformed to give salts of 1,2,3,4-tetrahydro-6-methyl-1-phenylpyridine. By the reduction of 6-phenylamino-2-hexanone with tin and hydrochloric acid, Lipp obtained 2-methyl-1-phenylpiperidine. Markwalder [27] showed that, in a similar way, attempts made to isolate the free base from the hydrobromide of 2-methyl-1-phenyl-2-pyrroline lead to hydrolytic opening of the pyrroline ring and formation of 5-phenylamino-2-pentanone, which, under the action of acids, is again converted into salts of 2-methyl-1-phenyl-2-pyrroline. By the reduction of 5-phenylamino-2-pentanone by means of tin and hydrochloric acid, 2-methyl-1-phenylpyrrolidine was obtained.

On the basis of all these considerations it may be supposed that the formation of 1-phenylpyrrolidine and N-2-butenylaniline in the reduction of 1-phenylpyrrole proceeds in the following way. 1-Phenylpyrrole (I) is first reduced to 1-phenyl-2-pyrroline (II), which, on the one hand, unites with two atoms of hydrogen giving 1-phenylpyrrolidine (III) and, on the other hand, undergoes hydrolytic decyclization with formation of γ-phenylaminobutyraldehyde (IV). The aldehyde (IV) is reduced further to 4-phenylamino-1-butanol (V), which is dehydrated to give N-3-butenylaniline (VI), which isomerizes into N-2-butenylaniline (VII). 1-Phenylpyrrolidine (III) can be formed also in another way, namely by cyclodehydration of 4-phenylamino-1-butanol (V).

---

* A similar result was obtained by Mumm and Moller [25] in the hydrolysis of the benzoyl derivative of α-methylallylaniline. Instead of the expected α-methylallylaniline, a hydroxy amine of composition of $C_{10}H_{15}ON$ was obtained.

It may be supposed that aniline is formed by the splitting of N-2-butenylaniline by hydrogenation. Further experimental study of the reaction will be necessary in order to determine whether this explanation of the mechanism of the reduction of 1-phenylpyrrole is correct.



EXPERIMENTAL

Preparation of 1-Phenylpyrrole

Expt. 1. Mucic acid (42 g; 0.2 mole) was added with constant stirring to aniline (37.2 g; 0.4 mole) heated to 150-160°. The mixture was heated at 140-150° for 1 hr and was allowed to stand for several days. It had then grown hard and readily broke down into a light-yellow powder. The aniline mucate obtained was carefully ground with aluminum oxide (42 g), and the mixture was transferred to a 200 ml round-bottomed flask fitted with a condenser arranged for distillation. The flask was heated on an oil bath. Distillation commenced at a bath temperature of 250° and terminated at 340°. The main portion of the distillate came over at a bath temperature of 270-320°. A residue of aluminum oxide impregnated with resin remained in the flask. The distillate was acidified with dilute hydrochloric acid, and the 1-phenylpyrrole was steam-distilled off, filtered off, washed with water, and dried in a desiccator over sulfuric acid (15.8 g; 56%. M.p. 58-59°). M.p. after sublimation: 61-62°.

Expt. 2. Aniline mucate was prepared from mucic acid (42 g; 0.2 mole) as in expt. 1. The salt obtained was introduced into a 200 ml round-bottomed flask, which was heated on an oil bath. Distillation commenced at 220° and finished at 320°. 1-Phenylpyrrole was isolated from the distillate as described above (11.8 g; 42%. M.p. 58-59°).

Reduction of 1-Phenylpyrrole by Means of Zinc Dust in Conjunction with Hydrochloric and Acetic Acids at 50-65°

Zinc dust (120 g) and conc. HCl (120 g) were added in small portions with energetic shaking to a solution of 1-phenylpyrrole (20 g) in glacial acetic acid (200 ml). The temperature of the reaction mixture was constantly maintained within the range 50-65°. Addition of zinc and hydrochloric acid occupied $1\frac{1}{2}$ hr. During the following $1\frac{1}{2}$ hr, the reaction mixture was agitated vigorously and was warmed on the water-bath to 50-65°. The mixture was then cooled, rendered alkaline with caustic soda, and steam-distilled. The yellow oil that went over into the distillate was extracted with ether, and the ether extract was dried over fused caustic potash. The ether was driven off, and the residue was dried by means of barium oxide at 110-120° for 6 hrs and then fractionated at 6 mm. The following fractions were obtained:

Fraction 1, b.p. to 100° – 1.3 g
Fraction 2, b.p. 100-102.5° – 4.7 g; d_4^{20} 0.9792; n_D^{20} 1.5648
Fraction 3, b.p. 102.5-105° – 1.2 g

Analysis of Fraction 2

Found %: C 81.93; 81.95; H 8.79; 8.81; N 9.50; 9.36
$C_{10}H_{13}N$. Calculated %: C 81.59; H 8.90; N 9.51
$C_{10}H_{11}N$. Calculated %: C 82.71; H 7.64; N 9.65

In order to obtain sufficient material, the reduction of 1-phenylpyrrole under these conditions was repeated several times. When the steam-distilled and dried product of the reduction reaction was vacuum-distilled, the fraction of b.p. 92-102° at 5 mm was collected, and this was subjected to further investigation.

Benzoylation of the Fraction of b.p. 92-102° (5 mm). The substance (16 g) was emulsified in 10% caustic soda solution (70 ml), and over an hour with vigorous agitation benzoyl chloride (14 g) was added in 5 portions. The excess of benzoyl chloride was hydrolyzed by warming. The upper layer (a mixture of an oil and a crystalline substance) was separated, washed with water, and then extracted with 10% hydrochloric acid. The crystalline substance was filtered off, washed with water, and dried in a desiccator over sulfuric acid.

Isolation of 1-Phenylpyrrolidine. The hydrochloric acid extract, the filtrate, and the washings were united. The resulting solution was rendered alkaline by means of caustic soda, and the oil that separated was extracted with ether. The ether extract was dried by means of fused caustic potash. The residue remaining after the ether had been driven off was vacuum-distilled. The product was 1-phenylpyrrolidine (8.6 g) having the following constants: b.p. 129-131° at 16 mm; d_4^{20} 1.0172; n_D^{20} 1.5839.

Picrate of 1-Phenylpyrrolidine. A warm ethereal solution of picric acid (2.29 g; 0.01 mole) was added to an ethereal solution of 1-phenylpyrrolidine (1.47 g; 0.01 mole). A finely crystalline precipitate of the picrate immediately began to appear. It was filtered off and washed with ether (3.64 g; m.p. 114-115°). M.p. after recrystallization from ethanol: 116-117°.

1-Phenylpyrrolidine prepared by us from 1,4-dibromobutane and aniline had the following constants: b.p. 129-130° at 16 mm; d_4^{20} 1.0145; n_D^{20} 1.5820. The picrate prepared from this preparation and recrystallized from ethanol melted at 116-117°. In admixture with the picrate of 1-phenylpyrrolidine obtained by the reduction of 1-phenylpyrrole it melted without depression.

The Benzoyl Derivative of N-2-Butenylaniline. The crystalline benzoylation product (11 g) melted at 83-89°. After three recrystallizations from ethanol, 6.8 g of the benzoyl derivative of N-2-butenylaniline, m.p. 90-91°, was obtained.

Found %: C 81.08; 81.05; H 6.91; 6.96; N 5.48; 5.28
$C_{17}H_{17}ON$. Calculated %: C 81.24; H 6.82; N 5.57

The benzoyl derivative of N-2-butenylaniline readily dissolves on warming in ethanol, benzene, acetone, and ether; it crystallizes in prisms from ethanol. The N-2-butenylaniline prepared by one of us [15] by the reduction of 3,6-dihydro-2-phenyl-1,2,2H-oxazine with sodium and alcohol was benzoylated. The benzoyl derivative, after recrystallization from ethanol, melted at 90-91°. In admixture with the benzoyl derivative of N-2-butenylaniline obtained by the reduction of 1-phenylpyrrole, it melted without depression.

Hydrolysis of the Benzoyl Derivative of N-2-Butenylaniline by means of Hydrochloric Acid. The benzoyl derivative (10 g) and conc. HCl (100 ml) were introduced into a flask fitted with a reflux condenser. The mixture was boiled for 12 hrs. It was then cooled, diluted twice with water, and the benzoic acid was extracted with ether. The acid solution was rendered alkaline with caustic soda, and the oil that separated was extracted with ether. The ether extract was dried with fused caustic potash. The residue after removal of ether was distilled over under 12 mm pressure. The following fractions were collected:

Fraction 1, b.p. to 155° – 1.6 g
Fraction 2, b.p. 155-165° – 3.1 g

Fraction 2 partially crystallized out. The crystals were filtered off and washed with absolute ether. A substance (2.0 g) of m.p. 59-61° was obtained. M.p. after recrystallization from ethanol: 60.5-61.5°.

Found %: C 73.06; 73.10; H 9.22; 9.06; N 8.24; 8.07
$C_{10}H_{15}ON$. Calculated %: C 72.69; H 9.15; N 8.48

Hydrolysis of the Benzoyl Derivative of N-2-Butenylaniline with Alcoholic Alkali. The benzoyl derivative (8 g) and a solution of caustic potash (5 g) in isoamyl alcohol (20 ml) were introduced into a flask fitted with reflux condenser. The mixture was boiled for 3 hrs. The contents of the flask were cooled and diluted with ether; potassium benzoate was extracted with water. The ethereal solution was extracted with 20% hydrochloric acid. The acid extract was washed with ether, rendered alkaline with caustic soda, and the oil that separated was extracted with ether. The ethereal solution was dried with fused caustic potash, the ether was driven off, and the residue was fractionated. N-2-Butenylaniline (1.5 g) was obtained; it had the following constants: b.p. 93-95° at 4 mm; d_4^{20} 0.9573; n_D^{20} 1.5554. N-2-Butenylaniline prepared from 3,6-dihydro-2-phenyl-1,2,2H-oxazine [15] had the following constants: b.p. 89-90° at 3 mm; d_4^{20} 0.9613; n_D^{20} 1.5587.

Reduction of 1-Phenylpyrrole by means of Zinc Dust in conjunction with Hydrochloric and Acetic Acids at 40-50°

Zinc dust (100 g) and conc. HCl (100 ml) were added in small portions at a time over $1\frac{1}{2}$ hr with vigorous agitation to a solution of 1-phenylpyrrole (20 g) in glacial acetic acid (200 ml). The temperature of the reaction mixture was maintained in the range 40-50°. During the following $1\frac{1}{2}$ hr, the reaction mixture was vigorously agitated and kept at 40-50° on a water-bath. The mixture was cooled, made alkaline with caustic soda, and steam-distilled. Further treatment was carried out as in the previous experiment. In the fractionation of the reduction product under 4 mm pressure, the following fractions were collected:

Fraction 1, b.p. to 92° – 1.4 g
Fraction 2, b.p. 92-96° – 8.1 g

Benzoylation of Fraction 1. The substance (1.4 g) was emulsified in 10% caustic soda solution (10 ml). Benzoyl chloride (2.1 g) was added to the emulsion, and the mixture was agitated for 20 min. The crystalline benzoylation product was filtered off, washed with water, and dried in a desiccator over sulfuric acid (2.5 g; m.p. 145-155°). After four recrystallizations from ethanol, 1.2 g of benzanilide, m.p. 162-163°, was obtained.

Found %: C 79.06; 79.33; H 5.62; 5.69; N 6.82; 6.79
$C_{13}H_{11}ON$. Calculated %: C 79.16; H 5.62; N 7.10

Benzoylation of Fraction 2. The substance (8.0 g) was emulsified in a 10% solution of caustic soda (50 ml), and benzoyl chloride (7.0 g) was added to the emulsion with agitation in three portions. From the reaction products, 1-phenylpyrrolidine (5.4 g) and the benzoyl derivative of N-2-butenylaniline (2.7 g; m.p. 90-91°) were isolated.

Reduction of 1-Phenylpyrrole by means of Zinc Dust and Hydrochloric Acid at 60-75°

Zinc dust (50 g) was added in small portions at a time with vigorous shaking to an emulsion of 1-phenylpyrrole (20 g) in conc. HCl (100 ml) heated to 65°. The zinc dust was added over 4 hrs. Then, further zinc dust (100 g) and conc. HCl (300 ml) were added over 4 hrs. The temperature of the mixture was maintained constantly in the range 60-75°. The reaction mixture was cooled, made alkaline with caustic soda, and steam-distilled. Further treatment was carried out as in the previous experiments. As a result of fractionation at 3 mm, the following fractions were obtained:

Fraction 1, b.p. to 90° – 1.0 g
Fraction 2, b.p. 90-92° – 4.4 g; d_4^{20} 0.9903; n_D^{20} 1.5692
Fraction 3, b.p. above 92° – 0.8 g

Analysis of Fraction 2

Found %: C 81.88; 81.62; H 8.88; 8.77; N 9.52; 9.66
$C_{10}H_{13}N$. Calculated %: C 81.59; H 8.90; N 9.51
$C_{10}H_{11}N$. Calculated %: C 82.71; H 7.64; N 9.65

From the benzoylation products in Fraction 2, 1-phenylpyrrolidine and the benzoyl derivative of N-2-butenylaniline, m.p. 90-91°, were isolated.

SUMMARY

1. An investigation has been made into the reduction of 1-phenylpyrrole by means of zinc dust and hydrochloric acid at 60-75° and by means of zinc dust in conjunction with hydrochloric and acetic acids at 40-50° and at 50-65°.

2. It has been found that, when 1-phenylpyrrole is reduced under the conditions used in this work, it unites with four atoms of hydrogen with formation of 1-phenylpyrrolidine and N-2-butenylaniline.

3. An explanation has been proposed for the mechanism of the reduction of 1-phenylpyrrole involving the intermediate formation of 1-phenyl-2-pyrroline.

Received December 1, 1951

Institute of Organic Chemistry of the
USSR Academy of Sciences and the
M. V. Lomonosov Moscow State University

LITERATURE CITED

[1] G. Ciamician, M. Dennstedt, Ber. 16, 1536 (1883); G. Ciamician, Ber. 34, 3951 (1901).

[2] L. Knorr, P. Rabe, Ber. 34, 3489 (1901); see also L. Andrews, McElvain, J. Am. Chem. Soc. 51, 889 (1929).

[3] N. D. Zelinsky and Yu. K. Yuryev. J. Gen. Chem. 1, 1 (1931).

[4] G. Ciamician, P. Magnaghi, Ber. 18, 725 (1885).

[5] H. Fischer, H. Hofelmann, Z. physiol. Chem. 251, 187 (1938).

[6] A. Treibs, D. Dinelli, Lieb. Ann. 517, 170 (1935).

[7] A. Sohn, Ber. 68, 148 (1935).

[8] A. Sohn, Ber. 72, 2150 (1939).

[9] H. P. L. Gitsels, J. P. Wibaut, Rec. Trav. Chim. 59, 1093 (1940); 60, 50 (1941).

[10] J. P. Wibaut, J. Dhont, Rec. Trav. Chim. 62, 272 (1943); J. Dhont, J. P. Wibaut, Rec. Trav. Chim. 63, 81 (1944).

[11] J. P. Wibaut, J. Th. Hackmann. Rec. Trav. Chim. 51, 1157 (1932).

[12] E. Spath, J. P. Wibaut, F. Kesztler, Ber. 71, 100 (1938).

[13] P. G. Haines, A. Eisner, J. Am. Chem. Soc. 72, 1719 (1950).

[14] F. E. King, J. R. Marshall, P. Smith, J. Chem. Soc. 1951, 239.

[15] Yu. A. Arbuzov. Rep. Acad. Sci. USSR 63, 531 (1948); Bull. Acad. Sci. USSR. Div. Chem. Sci., No. 3, 547 (1952). See Consultants Bureau English Translation, p. 523.

[16] M. Kottnitz, J. prak. Chem. [2], 6, 136 (1872).

[17] F. Feist, Ber. 35, 1654 (1902).

[18] A. Pictet, Steinmann, Ber. 35, 2529 (1902).

[19] L. C. Craig, R. M. Hixon, J. Am. Chem. Soc. 52, 804 (1930).

[20] H. Adkins, H. L. Coonradt, J. Am. Chem. Soc. 63, 1556 (1941).

[21] F. F. Blicke, J. L. Powers, J. Am. Chem. Soc. 66,304 (1944).

[22] M. de Jong, J. P. Wibaut, Rec. Trav. Chim. 49, 243 (1930).

[23] F. K. Signaigo, H. Adkins, J. Am. Chem. Soc. 58, 709 (1936).

[24] A. E. Chichibabin, Ber., 56, 1746 (1923).

[25] O. Mumm, F. Moller, Ber. 70, 2214 (1937).

[26] A. Lipp. Lieb. Ann. 289. 173 (1896).

[27] J. Markwalder, J. prak. Chem. [2] 75, 329 (1907).

[28] G. G. Evans, J. Am. Chem. Soc. 73, 5230 (1951).

[29] E. E. Blaise, Comptes. rend. 158, 1686 (1914); E. E. Blaise, A. Cornillot, Comptes. rend. 178, 1617 (1924).

[30] J. P. Wibaut, H. C. Beyerman, Rec. Trav. Chim. 70, 977 (1951).

BRIEF COMMUNICATIONS

SYNTHESIS AND PROPERTIES OF ALLYLSILANES: TRIALLYL-α-NAPHTHYLSILANE, TRIALLYLCYCLOHEXYLSILANE, TRIALLYLBUTYLSILANE, AND ALLYLTRIBUTYLSILANE

A. D. Petrov and L. L. Shchukovskaya

Sila-hydrocarbons of the type $(CH_2=CH-CH_2)_x \cdot SiR_{4-x}$ are of considerable interest because of the comparative ease with which they polymerize and undergo copolymerization [1] with vinyl-type compounds (styrene, vinyl chloride, acrylates). However, very few representatives of this series have yet been synthesized; also, all the known sila-hydrocarbons contain only aliphatic radicals (R). Whitmore [2] obtained $(CH_2=CH-CH_2) \cdot Si(CH_3)_3$; Yakovlev [3] $(CH_2=CH-CH_2)_2 \cdot Si(C_2H_5)_2$; Petrov and Mironov [4] $(CH_2=CH-CH_2) \cdot Si(C_2H_5)_3$; Post [5] $HSi(CH_2-CH=CH_2)_3$ and in one U.S. patent [6], a description is given of the synthesis and properties of $Si(CH_2-CH=CH_2)_4$ (b.p. 102-103° at 15 mm; d_4^{20} 0.8353; n_D^{20} 1.4864).

EXPERIMENTAL

In this investigation we have prepared for the first time the allylsilanes indicated above, and we have also repeated the synthesis of $Si(CH_2-CH=CH_2)_4$. In the first two syntheses we used the usual method for the preparation of sila-hydrocarbons – via an alkyl- or aryl-magnesium halide, the reaction being begun in ether and completed by heating in ligroin (fraction of b.p. 130-160°). In subsequent syntheses the reaction was carried out in ether.

Triallyl-α-naphthylsilane α-$C_{10}H_7Si(CH_2-CH=CH_2)_3$. Triethoxy-α-naphthylsilane α-$C_{10}H_7Si(OC_2H_5)_3$ and allyl bromide, taken in a molar ratio of 1:4, were poured into absolute ether containing magnesium. After the complex had been broken down by means of ammonium chloride, a sila-hydrocarbon containing 35% of the initial triethoxynaphthylsilane was obtained. The pure sila-hydrocarbon was obtained only after a further treatment with allylmagnesium bromide and heating in ligroin. Yield 60% of theoretical.

Triallylcyclohexylsilane $C_6H_{11}Si(CH_2-CH=CH_2)_3$. This was synthesized in the same way. Yield 42% of theoretical. The original cyclohexyltriethoxysilane $(C_6H_{11}Si(OC_2H_5)_3$ had the following constants: b.p. 101-102° at 7 mm; n_D^{20} 1.4280; d_4^{20} 0.9444.

Found %: C 58.44; 58.69; H 10.72; 10.54; Si 11.32; 11.57
$C_{12}H_{28}SiO_3$. Calculated %: C 58.49; H 10.64; Si 11.39

Triallylbutylsilane $C_4H_9Si(CH_2-CH=CH_2)_3$. This was prepared by the action of n-butyltrichlorosilane on allylmagnesium bromide. After the ether had been driven off, the residue in the flask was heated on a boiling water bath. The reaction product was decomposed with ammonium chloride, and the sila-hydrocarbon was purified by heating with metallic sodium on the water-bath. Yield 54% of theoretical.

Allyltributylsilane $(n\text{-}C_4H_9)_3Si\ CH_2-CH=CH_2$. This was prepared by adding a mixture of allyl bromide and tributylchlorosilane to magnesium. The product was purified as indicated above. Yield 74% of theoretical.

Tributylchlorosilane $(n\text{-}C_4H_9)_3SiCl$. This was synthesized by Whitmore's method [7]; the yield was 74.2%; b.p. 124.5° at 8 mm; n_D^{20} 1.4471; d_4^{20} 0.8768.

Found %: Cl 14.57; 14.47
$(n\text{-}C_4H_9)_3SiCl$. Calculated %: Cl 15.09

Hexabutyldisiloxane had the following properties: b.p. 198-200° at 12 mm; n_D^{20} 1.4455; d_4^{20} 0.8553.

Found %: Si 13.84
$n\text{-}(C_4H_9)_6Si_2O$. Calculated %: Si 13.52

TABLE

Properties of Allylsilanes

α-$C_{10}H_7Si(CH_2-CH=CH_2)_3$ b.p. 194-195° at 10 mm; n_D^{20} 1.5872; d_4^{20} 0.9928	Found %: C 81.56; 81.55; H 8.36; 8.16; Si 10.09; 10.13 $C_{19}H_{22}Si$. Calculated %: C 81.95; H 7.96; Si 10.09
$C_6H_{11}Si(CH_2-CH=CH_2)_3$ b.p. 127-129° at 13 mm; n_D^{20} 1.4790; d_4^{20} 0.8659; MR_D(found) 76.7; MR_D(calcd) 77.36	Found %: C 77.08; H 11.81; Si 11.18 $C_{15}H_{26}Si$. Calculated %: C 76.92; H 11.10; Si 12.0
n-$C_4H_9Si(CH_2-CH=CH_2)_3$ b.p. 108° at 11 mm; n_D^{20} 1.4722; d_4^{20} 0.8200; MR_D (found) 71.05; MR_D (calcd) 70.33	Found %: C 75.31; H 11.67; Si 12.91 $C_{13}H_{24}Si$. Calculated %: C 75.0 ; H 11.54; Si 13.46
$(n-C_4H_9)_3SiCH_2-CH=CH_2$ b.p. 145° at 12 mm; n_D^{20} 1.4534; d_4^{20} 0.8031; MR_D (found) 80.83; MR_D (calcd) 80.50	Found %: C 74.73; 74.77; H 13.48; 13.50; Si 10.78; 11.18 $C_{15}H_{32}Si$. Calculated %: C 75.0; H 13.30; Si 11.66
$Si(CH_2-CH=CH_2)_4$ b.p. 90.5° at 10 mm; n_D^{20} 1.4840; d_4^{20} 0.8345; MR_D (found) 65.82; MR_D (calcd) 65.25	Found %: C 75.80; 75.63; H 10.66; 10.74 $C_{12}H_{20}Si$. Calculated %: C 75.0 ; H 10.04

Tetraalylsilane $Si(CH_2-CH=CH_2)_4$ was prepared by adding a mixture of tetrachlorosilane and allyl iodide to magnesium. The ether was driven off, and the product was distilled off without first breaking down the complex. Yield 37% of theoretical. The properties of the silanes that we prepared are given in the table.

Received November 5, 1951

Institute of Organic Chemistry of the
USSR Academy of Sciences

LITERATURE CITED

[1] Chem. Abs. 43, 1223 (1949); J. Pyle 2448391; Chem. Abs. 42, 4795 (1948); C. A. Mckenzie, I. Rust.

[2] L. Sommer, L. Tyler, F. Whitmore, J. Am. Chem. Soc. 70, 2872 (1948).

[3] V. I. Yakovlev. J. Gen. Chem. 19, 1969 (1949).*

[4] A. D. Petrov and V. F. Mironov. Proc. Acad. Sci. USSR 75, No. 5, 707 (1950).

[5] J. Jenkins, N. Lavery, P. Gunther, H. Post, J. Org. Chem. 13, 862-866 (1948).

[6] Amer. Cyanamide Co. U.S. P. 2381793 (1945); H. Post, Silicones, p. 186.

[7] F. Whitmore, L. Sommer, P. Digiorgio. W. Strong, J. Am. Chem. Soc. 68, 1380 (1946).

---

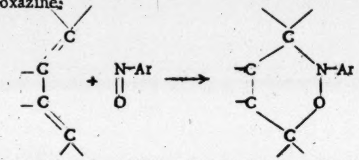
* No report by Yakovlev appears in the 1949 Volume of J. Gen. Chem. Reference is evidently to another Journal. - Publisher.

THE REACTIONS OF DIENIC HYDROCARBONS WITH NITROSO COMPOUNDS

ADDITION OF 2,3-DIMETHYL-1,3-BUTADIENE, OF 1-PHENYL-1,3-BUTADIENE, AND OF BI-1-CYCLOHEXEN-1-YL TO AROMATIC NITROSO COMPOUNDS

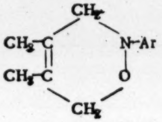
Yu. A. Arbuzov, N. L. Fedyukina, V. V. Shabyrina, and R. I. Shepeleva

In the previous papers [1,2] it was shown that 1,3-butadiene, 1,3-pentadiene, and 2,4-hexadiene add on to aromatic nitroso compounds according to the scheme of the diene synthesis with formation of derivatives of 3,6-dihydro-1,2,2H-oxazine:

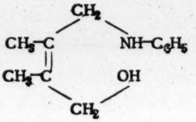


It was to be expected that the addition reaction between dienic hydrocarbons and nitroso compounds leading to the formation of 3,6-dihydro-1,2,2H-oxazine derivatives would have a general character. The experimental data that we bring forward in this paper confirm this supposition.

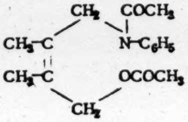
We have prepared addition products of aromatic nitroso compounds with 2,3-dimethyl-1,3-butadiene, trans-1-phenyl-1,3-butadiene, and bi-1-cyclohexen-1-yl. In the experiments in which 2,3-dimethyl-1,3-butadiene was added to nitroso compounds, ether was used as solvent. Two compounds were formed in the reaction between 2,3-dimethyl-1,3-butadiene and nitrosobenzene. The first is almost insoluble in ether and consists of colorless glistening needles, m.p. 153-155° (dec.). This substance begins to separate on the walls of the reaction flask soon after the addition of the dimethylbutadiene to the ethereal solution of nitrosobenzene, while the reaction mixture still has a green color. The nature of the substance of m.p. 153-155° has not yet been established. The second substance, which is 3,6-dihydro-4,5-dimethyl-2-phenyl-1,2,2H-oxazine (Ia), is soluble in ether. This substance was obtained in 66% yield and has b.p. 125-126° at 3 mm and m.p. 39.5-40.5°. The reduction of 3,6-dihydro-4,5-dimethyl-2-phenyl-1,2-2H-oxazine (Ia) with zinc dust and glacial acetic acid leads to the formation of 2,3-dimethyl-4-phenylamino-2-buten-1-ol (II), b.p. 154.5-155° at 2 mm. Acetylation of the amino alcohol (II) with acetic anhydride gives the diacetyl derivative (III), which has b.p. 157-158° at 1 mm.



(Ia) Ar = phenyl
(Ib) Ar = p-tolyl



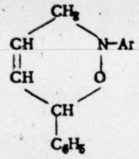
(II)



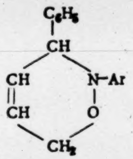
(III)

In the reaction between 2,3-dimethyl-1,3-butadiene and p-nitrosotoluene, the reaction conditions being the same as in the reaction with nitrosobenzene, the ether-insoluble substance was not obtained. From the reaction products, 3,6-dihydro-4,5-dimethyl-2-(p-tolyl)-1,2,2H-oxazine (Ib), m.p. 62-63°, was isolated with a yield of 55%.

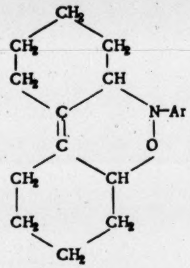
The reaction of 1-phenyl-1,3-butadiene with nitrosobenzene was carried out in ethanol and in pyridine. When an ethanol medium was used, the adduct (IVa or Va), m.p. 84.5-85°, was obtained with a yield of 85%. When a pyridine medium was used, the yield of the adduct was only 55%. In the reaction of 1-phenyl-1,3-butadiene with o-nitrosotoluene in ethanol, an adduct (IVb or Vb), m.p. 46-47°, was obtained in 80% yield. In the reaction of 1-phenyl-1,3-butadiene with p-nitrosotoluene in ethanol solution, an 80% yield of the adduct (IVc) or (Vc), m.p. 66-67°, was obtained.



(IVa) Ar = phenyl
(IVb) Ar = o-tolyl
(IVc) Ar = p-tolyl



(Va) Ar = phenyl
(Vb) Ar = o-tolyl
(Vc) Ar = p-tolyl



(VIa) Ar = phenyl
(VIb) Ar = p-tolyl

The first experiments on the addition of bi-1-cyclohexen-1-yl to nitroso compounds were carried out in pyridine. In the reaction of bicyclohexenyl with nitrosobenzene, a 26% yield was obtained of 1,2,3,4,4a,6a,7,8,9,10-decahydro-6-phenyl-6H-dibenz[c,e]-o-oxazine (VIa), m.p. 100-101°. In the reaction of bicyclohexenyl with p-nitrosotoluene, a 30% yield was obtained of 1,2,3,4,4a,6a,7,8,9,10-decahydro-6-(p-tolyl)-6H-dibenz[c,e]-o-oxazine (VIb), m.p. 103.5-104.5°. In later experiments, ethanol was used as solvent, and in these the adduct from bicyclohexenyl and nitrosobenzene was obtained with a yield of 43%, and the adduct of p-nitrosotoluene was obtained in a yield of 40%.

The adducts of nitrosobenzene with 2,3-dimethyl-1,3-butadiene and with 1-phenyl-1,3-butadiene were prepared in 1947 by Wichterle [3], but this author erroneously ascribed the structure denoted by 1,5-dimethyl-3-phenyl-6-oxa-3-azabicyclo [3.1.0] hexane to the addjuct formed with dimethylbutadiene, and the structure denoted by 2,3-diphenyl-6-oxa-3-azabicyclo [3.1.0] hexane to the adduct formed with phenylbutadiene.

EXPERIMENTAL

3,6-Dihydro-4,5-dimethyl-2-phenyl-1,2,2H-oxazine (Ia)

Nitrosobenzene (21.4 g = 0.2 mole), ether (300 ml), and 2,3-dimethyl-1,3-butadiene (16.4 g = 0.2 mole) were introduced into a flask, which was then placed in ice. After some time, pale-yellow needle-like crystals began to appear on the walls of the flask. After one day, the solution had acquired an orange color. The crystals were filtered off and washed with absolute ether. 4.6 g of substance was obtained. After recrystallization from ethanol, colorless glistening needles, m.p. 153-155° (dec.), were obtained.

Found %: C 74.01; 73.85; H 6.57; 6.60; N 9.07; 9.17

The ether was driven off from the filtrate, and the residue was vacuum-distilled. 3,6-Dihydro-4,5-dimethyl-2-phenyl-1,2,2H-oxazine (25.0 g, 66%) b.p. 125-126° at 3mm was obtained. After one recrystallization from ethanol, a colorless finely crystalline substance, m.p. 39.5-40.5° was obtained.

Found %: C 76.44; 76.62; H 8.16; 8.29; N 7.38; 7.27
$C_{12}H_{15}ON$. Calculated %: C 76.15; H 7.99; N 7.40

2,3-Dimethyl-4-phenylamino-2-buten-1-ol (II)

A solution of 3,6-dihydro-4,5-dimethyl-2-phenyl-1,2,2H-oxazine (18.9 g = 0.1 mole) in glacial acetic acid (200 ml) was introduced into a bottle, and zinc dust (20 g) was added. The bottle was closed with a stopper and shaken vigorously for 10 min; more zinc dust (20 g) was then added, and the bottle was shaken for a further 15 min. The reaction mixture was diluted with 200 ml of water, and caustic soda (200 g) was added. The resulting alkaline solution was steam-distilled to remove substances that were volatile in steam; 0.75 liter of distillate was collected. The solution remaining in the flask was filtered hot from the precipitate present. The filtrate was cooled and extracted 4 times with benzene (4·100 ml). The benzene extract was washed with water, the benzene was driven off, and the residue was fractionated under reduced pressure. The product was 2,3-dimethyl-4-phenylamino-2-buten-1-ol (13.3 g, 70%), with the following constants:b.p. 154.5-155° at 2 mm; d_4^{20} 1.0501; n_D^{20} 1.5744; found MR_D 60.22; calculated MR_D 58.68; EMR_D 1.54. The substance is an almost colorless very viscous liquid, which yellows on standing.

Found %: C 75.09; 75.07; H 9.29; 9.05; N 7.29; 7.35
$C_{12}H_{17}ON$. Calculated %: C 75.35; H 8.96; N 7.32

Diacetyl Derivative of 2,3-dimethyl-4-phenylamino-2-buten-1-ol (III)

A solution of 2,3-dimethyl-4-phenylamino-2-buten-1-ol (9.56 g, 0.05 mole) in 40 ml acetic anhydride was introduced into a flask fitted with a reflux condenser. The flask was heated on a boiling water bath for 4 hours, and acetic acid and excess acetic anhydride were then distilled off under reduced pressure; the residue was distilled. The diacetyl derivative of 2,3-dimethyl-4-phenylamino-2-buten-1-ol (13.05 g, 95% of theoretical) obtained had the following constants: b.p. 157-158° at 1 mm; d_4^{20} 1.0774; n_D^{20} 1.5237; found MR_D 78.14; calculated MR_D 77.27; EMR_D 0.87. It is a colorless, very viscous liquid.

Found %: C 69.81, 70.01; H 8.09, 8.07; N 5.04, 5.23
$C_{16}H_{21}O_3N$. Calculated %: C 69.79; H 7.69; N 5.09

3,6-Dihydro-4,5-dimethyl-2-(p-tolyl)-1,2,2H-oxazine (Ib)

p-Nitrosotoluene (18.16 g, 0.15 mole), 220 ml ether, and 2,3-dimethyl-1,3-butadiene (12.3 g, 0.15 mole) were introduced into a flask, which was placed in ice for one day. The ether was then driven off, and the residue was steam-distilled. A slightly yellowish crystalline substance came over in the distillate, and it was filtered off and dried. 3,6-dihydro-4,5-dimethyl-2-(p-tolyl)-1,2,2H-oxazine (16.5 g, 54% of theoretical) was obtained (m.p. 60-62°). After one recrystallization from ethanol, colorless fine crystals, m.p. 62-63°, were obtained.

Found %: C 76.90, 77.03; H 8.64, 8.59; N 7.08, 7.17
$C_{13}H_{17}ON$. Calculated %: C 76.81; H 8.43; N 6.89

3,6-Dihydro-2,6 (or 2,3)-diphenyl-1,2,2H-oxazine (IVa or Va)

Expt. 1. A solution of nitrosobenzene (17.1 g, 0.16 mole) in 200 ml ethanol was cooled in ice, and 26.6 g of trans-1-phenyl-1,3-butadiene was added. After an hour, colorless needles began to separate, and the amount formed gradually increased. By the next day, the reaction solution had acquired a pale-yellow color. The crystalline substance was filtered off and washed with alcohol and ether. An adduct (30.4 g) of m.p. 82-83° was obtained. A further quantity (2.0 g) of the adduct was obtained from the mother liquor. Total yield 32.4 g (85% of theoretical). M.p. after one recrystallization from ethanol was 84.5-85°.

Found %: C 81.22, 81.18; H 6.46, 6.46; N 5.98, 6.08
$C_{16}H_{15}ON$. Calculated %: C 80.98; H 6.37; N 5.90

Expt. 2. An ice-cooled solution of nitrosobenzene (6.5 g, 0.06 mole) in 45 ml pyridine was added to an ice-cooled solution of trans-1-phenyl-1,3-butadiene (7.9 g, 0.06 mole) in 45 ml pyridine. The flask was placed in ice overnight.* The pyridine was distilled off under reduced pressure. After two recrystallizations from ethanol, the adduct (7.9 g) was obtained in the form of yellowish needles, m.p. 82-83°, yield 55% of theoretical.

3,6-Dihydro-2-phenyl-6 (or 3)-(o-tolyl-1,2,2H-oxazine (IVb or Vb)

trans-1-Phenyl-1,3-butadiene (6.5 g, 0.05 mole) was added to an ice-cooled solution of o-nitrosotoluene (6.1 g, 0.05 mole) in 80 ml ethanol. The flask was placed in ice for one day. A considerable quantity of colorless needle-like crystals separated. The adduct was filtered off and washed with cold ethanol. The yield of adduct was 10.1 g (80% of theoretical). M.p. after recrystallization from a mixture of ethanol and light petroleum was 46-47°.

Found %: C 81.52, 81.57; H 6.94, 6.89; N 5.66, 5.67
$C_{17}H_{17}ON$. Calculated %: C 81.21; H 6.84; N 5.57

3,6-Dihydro-2-phenyl-6 (or 3)-(p-tolyl)-1,2,2H-oxazine (IVc or Vc)

An ice-cooled solution of trans-1-phenyl-1,3-butadiene (11.3 g, 0.09 mole) in 25 ml ethanol was added to an ice-cooled solution of p-nitrosotoluene (9.7 g, 0.08 mole) in 100 ml ethanol. The flask containing the reaction mixture was placed in ice for 2 days. A large quantity of colorless needle-like crystals separated, and the reaction solution became light yellow. The crystals were filtered off and washed with cold alcohol. The yield of adduct was 16.1 g (80% of theoretical). M.p. after recrystallization from ethanol was 66-67°.

Found %: C 81.37, 81.46; H 6.96, 6.82; N 5.86, 5.86
$C_{17}H_{17}ON$. Calculated %: C 81.21; H 6.84; N 5.57

1,2,3,4,4a,6a,7,8,9,10-Decahydro-6-phenyl-6H-dibenz [c,e,]-o-oxazine (VIa)

Expt. 1. An ice-cooled solution of nitrosobenzene (10.7 g, 0.1 mole) in 50 ml pyridine was added over 30 minutes with shaker to an ice-cooled solution of bicyclohexenyl (16.2 g, 0.1 mole) in 10 ml pyridine. The flask containing the reaction mixture was left overnight in ice. The solution acquired an orange-red color after 3 hours. Next day the pyridine was driven off under reduced pressure. The resinous residue partially crystallized on standing. The crystals were filtered off and washed with cold alcohol and ether. The yield of adduct, which was of a yellowish color and had a m.p. of 99.5-100.5°, was 7.0 g (26% of theoretical). After one recrystallization from ethanol, colorless needles, m.p. 101-102°, were obtained.

---

*By the next day, the solution had become brown.

Found %: C 80.53, 80.53; H 8.74, 8.48; N 5.24, 5.29
$C_{18}H_{23}ON$. Calculated %: C 80.26; H 8.60; N 5.20

Expt. 2. Bicyclohexenyl (16.2 g, 0.1 mole), 100 ml ethanol, and nitrosobenzene (10.7 g, 0.1 mole) were introduced into a bottle, which was closed with a stopper and shaken mechanically at room temperature for 2 hours. The precipitated crystals of adduct were filtered off and washed with cold alcohol (the solution had become orange). Yield of adduct: 11.3 g; a further amount (0.2 g) was separated from the mother liquor. Total yield was 11.5 g (43% of theoretical), in the form of almost colorless crystals. M.p. after recrystallization from ethanol was 101-102°.

1,2,3,4,4a,6a,7,8,9,10-Decahydro-6-(p-tolyl)-6H-dibenz [c,e]-o-oxazine (VIb)

Expt. 1. An ice-cooled solution of p-nitrosotoluene (6.05 g, 0.05 mole) in 50 ml pyridine was added over 20 minutes with shaking to an ice-cooled solution of bicyclohexenyl(8.1 g, 0.05 mole) in 10 ml pyridine. The flask containing the reaction mixture was left overnight in ice. The solution became orange-red. The pyridine was driven off under reduced pressure. The resinous residue partly crystallized on standing. The crystalline substance was filtered off and washed with cold alcohol. The yield of adduct in the form of almost colorless crystals was 4.2 g (30%). After one crystallization from ethanol, colorless needles, m.p. 103.5-104.5°, were obtained.

Found %: C 80.50, 80.59; H 8.99; 8 99, 4.96, 4.88
$C_{19}H_{25}ON$. Calculated %: C 80.53 H 8.89; 4.94

Expt. 2. Bicyclohexenyl (6.5 g, 0.04 mole), 50 ml ethanol, and p-nitrosotoluene (4.8 g, 0.04 mole) were introduced into a bottle, which was closed with a stopper and shaken mechanically at room temperature for 2 hours. The crystals that separated were filtered off and washed with cold alcohol. Yield of adduct: 4.3 g. A further amount (0.2 g) was isolated from the filtrate. Total yield was 4.5 g (40% of theoretical). After one recrystallization from ethanol, the adduct melted at 103.5-104.5°.

SUMMARY

1. A study has been made of the reactions of 2,3-dimethyl-1,3-butadiene, trans-1-phenyl-1,3-butadiene, and bi-1-cyclohexen-1-yl with aromatic nitroso compounds.

2. The following adducts have been prepared: 2,3-dimethyl-1,3-butadiene with nitrosobenzene and with p-nitrosotoluene; trans-1-phenyl-1,3-butadiene with nitrosobenzene, with o-nitrosotoluene, and with p-nitrosotoluene; bi-1-cyclohexen-1-yl with nitrosobenzene and with p-nitrosotoluene.

Institute of Organic Chemistry of the USSR Academy of Sciences
and
M.V.Lomonosov Moscow State University

Received October 15, 1951

LITERATURE CITED

[1] Yu.A.Arbuzov. Proc.Acad.Sci.USSR, 60, 993 (1948); Bull.Acad.Sci.USSR, Div.Chem.Sci., No. 2, 344 (1952).*

[2] Yu.A.Arbuzov and N.L.Fedyukina. Proc.Acad.Sci.USSR., 60, 1173 (1948).

[3] O. Wichterle. Collect. Trav. chim. Czech., 12, 292 (1947)

---

* See Consultants Bureau translation, p. 339.

CURRENT EVENTS

SESSION OF THE DIVISION OF CHEMICAL SCIENCES DEVOTED TO THE 125TH ANNIVERSARY OF THE BIRTH OF N.N.BEKETOV

On January 26, 1952, at a joint session of the Division of Chemical Sciences of the USSR Academy of Sciences and the Committee on the History of Chemistry, a notable occasion was celebrated – the 125 th anniversary of the birth of N.N.Beketov.

"The contribution made by Russian chemists to world science," said Corresponding Member A. F. Kapustinsky when opening the celebration session, "is indeed an invaluable one. Well-merited fame is associated with the names of Mendeleev, creator of the Periodic Law, Butlerov, creator of the theory of the structure of organic compounds, Zinin, pioneer in the chemistry of aniline compounds, Klaus, foremost chemist in the field of the platinum metals and discoverer of ruthenium, Hess, founder of thermochemistry, and the 'cohort of the famous', which include Markovnikov, Zaitsev, and other foremost workers in our native chemical science.

"In celebrating the 125th anniversary of the birth of one of the greatest chemists of this brilliant period in the history of chemistry – Academician Nikolay Nikolaevich Beketov, founder of modern physical chemistry and a remarkable scientist, whose numerous works, particularly those on thermochemistry, are deserving of the highest praise – we render that which is due to his services as a pioneer and as a continuator of the work of Lomonosov."

A paper on the life and activities of Academician N.N.Beketov was read by Ya.I.Turchenko, a candidate for the doctorate at the Institute of the History of Science. He gave a brief biography of N.N.Beketov, from which it was evident that Beketov was in close touch with such celebrities of chemistry as Zinin, Butlerov, and Mendeleev. Zinin's influence had its effect in the molding of Beketov as a scientist, while his association with Professor Ilyenkov, a notable educator, helped him to acquire aptitude as a teacher. Beketov's aim was to work in St.Petersburg with the celebrated chemist Zinin, but this could not be arranged. As there was no available post for him in St.Petersburg, he was compelled to take up duties as an assistant lecturer at Kharkov University, where he worked for 32 years. As he was a talented lecturer, he enjoyed great popularity, and his lectures drew large audiences.

Beketov took an interest in the training of specialists for his native land: he organized practical work and scientific investigations for his students and gave also a supplementary lecture course entitled "The Relations between Physical and Chemical Phenomena". With the object of furthering science and providing training for chemists, Beketov secured the establishment of a physicochemical department in Kharkov University, and in 1865, 21 years before such courses were introduced into the curriculum of Western universities, he began to deliver a course in physical chemistry – the first since that given by Lomonosov.

At an international congress of chemists held in the sixties of the last century, the fundamental concepts of Lomonosov on atoms and molecules were formulated anew. After the congress, Beketov wrote: "It is clear that he was concerned with questions about the structure of matter in general and about the molecular and atomic changes that occur in matter. The originality and clarity of his views on this subject are most impressive; he had arrived by reasoning at a concept that took its place in science only a century later. It is therefore easy to see why his contemporaries not only failed to understand him, but even treated his ideas in hostile fashion."

Beketov reacted actively and warmly to the discoveries of his brilliant compatriots. In his correspondence with A.M.Butlerov, he rejoices at the latter's successes: "I thank you most heartily," he wrote to Butlerov, "for sending me your 'Introduction to the Study of Organic Chemistry'. Your book could not be more opportune, in this present transitional period. All of those here who are concerned with chemistry think very highly of your book; they fell upon it with eagerness, particularly as your name, so closely associated with recent progress and new trends in science, endows it with special authority."

He welcomed Mendeleev's periodic law with enthusiasm. "Much work and the mind of a genius was required for the development of this exact system. Dmitri Ivanovich, through his great insight, was led to make alterations in certain atomic weights, and, finally, the periodic system that he had created showed him that certain gaps existed in the sequence of atomic weights, and, with the boldness of the man who really believes in the law that he has discovered, he predicted the existence, and possibility of discovery, of the missing members of the series of elements... ....no law had hitherto existed in chemistry that would permit the prediction of the existence of this or that element of a particular atomic weight and having certain physicochemical properties. Such a law was discovered and developed in brilliant fashion by Dmitri Ivanovich."

In 1872, with Beketov's active participation, a society for experimental science was created at Kharkov University. Also, stated Turchenko, Beketov's scientific work was highly esteemed byZaitsev and Butlerov, who presented Beketov for election as a corresponding member of the Academy of Sciences. In their presentation address, made on November 8, 1877, it is stated that "Beketov undoubtedly holds one of the most honored places among senior Russian chemists. He commenced his scientific activity in 1853 and has continued it with constant success up to the present time. The outstanding feature of Professor Beketov's work is its concern with fundamental general questions of chemistry, that is to say, with those questions whose solution has special importance for the science."

After the death of the senior Russian chemist Zinin, Butlerov put forward the names of Mendeleev and Beketov as candidates for the vacant chair of chemistry and technology. However, the reactionary governing body actively opposed this proposition and put forward the name of Beilstein. Right up to his death, Butlerov fought for the honor of Russian science and of Russian scientists.

Beketov's world-view was formed under the favorable influence of the ideas of the revolutionary democrats —the classics of Russian philosophical thought—and it determined his completely negative attitude to the tsarist regime. The following note occurs in his manuscripts: " .... Is it possible that the monarchy, the army, the war, the police, and finally...(undecipherable)... the government, etc., are really necessary for the well-being of humanity ?" and the answer is given: "yes, they are as necessary as a bump on the forehead of a man who is falt(ering) in a space that is devoid of light."

Beketov characterized his attitude to socialists and communists in the following words: "When one knows in whose hands the fate of the people lies and how difficult it is under such conditions for the people to organize society for their own convenience and not for that of the government, it is impossible not to sympathize with every attempt to find sensible and acceptable (national) foundations for the social order. Everyone, of course, has heard of the socialists and communists, but everyone has also hastened to convince himself that these are local utopians without taking the trouble to become acquainted with these new tendencies."

Beketov's work in physical chemistry was discussed by Professor N.A.Izmail ov of Kharkov University. During the 60 years of his scientific activity — said Izmailov — Beketov witnessed the birth of a great many views in chemistry; some of them developed, others died. With very few exceptions, all Beketov's researches in physical chemistry were devoted to chemical affinity and to the way in which this affinity is determined by the properties of the elements. Beketov examined various aspects of the relation between structure and properties: 1) the thermodynamics of affinity, 2) the relation between the stability of compounds and the structure of the atoms, their volumes, and the changes in volume in the formation of the compounds, 3) the regularities to be observed in the heats of formation of compounds, 4) the energy of the elements and their structure. As a result of his examination of these properties, he established the exceptional reducing properties of aluminum.

In his doctorate thesis, the results of his investigations on the displacement of one element by another are brought together. In his physical chemistry course, he points out the limitations of Berthelot's principle, which does not permit a fall in temperature in a chemical process. Beketov asserted that "every chemical change occurring without the performance of external work proceeds only in the direction leading to the greatest evolution of heat, and every system tends to change into one that corresponds to the greatest evolution of heat." Beketov ended his analysis of Berthelot's principle with the words: "and for this reason, Berthelot's principle must, in any case, be regarded as incomplete and one-sided." Beketov introduced the concept of "decomposition pressure", which is close to the concept of "degree of dissociation"; he examined the conditions under which reactions proceed when one component is removed from the sphere of reaction; and he examined the effect of temperature on exothermic and endothermic reactions.

Beketov was not interested in the mere accumulation of facts; every experiment that he carried out was designed with the object of developing and confirming his views. He made a number of generalizations about heat effects. As an illustration of the great evolution of heat that occurs when compounds are formed with an accompanying high contraction in volume, he made a comparison of the heat changes and contractions occurring in the formation of chlorides, bromides, iodides, and oxides. Beketov established also the variability of the heat of reaction when one element is displaced by another, thus contradicting the assertions of certain chemists, who had declared it to be constant. He must be assigned priority for his treatment of heats of reaction, which he showed to follow an additive law.

Izmailov, in assessing Beketov's results from the point of view of modern concepts on atomic structure, the nature of the chemical bond, and bond strength, marveled at the insight of this scientist, who penetrated so deeply, on the basis of thermodynamic data, into the mechanism of the formation of compounds. On the basis of his theoretical researches, Beketov arrived at the correct explanation of the reducing effect of clays and developed the method of aluminothermy.

Having based his work on the relation between the chemical behavior of elements and their structures and properties, Beketov considered also the possibility of their undergoing change; he expressed the view, which is quite correct, that if atoms should be found to be divisible, then processes involving this divisibility would be quite different in character from chemical processes and would be accompanied by enormous changes in energy. He expressed this idea particularly clearly in his lectures on thermodynamics at Moscow University in 1890: "...we may suppose that elements were formed from matter that was still more dynamic than they are themselves and that they have retained some fraction of the energy that was evolved, probably in very large amount, in their formation."

Owing to his attitude toward the elements, he was prepared for the discovery of radioactivity, and took a great interest in it. In his article "The Energy of the Elements" he expressed completely correct views on the mechanism of radioactive changes, on the source of the energy in radioactive changes, and on the stability of the elements.

In conclusion, Izmailov said that Beketov's name had gone down in the history of science primarily as that of the founder of physical chemistry, one of the originators of the mass-action law, the founder of aluminothermy, the chemist who first opened up the question of the relation between the structure and the properties of the elements and solved it in his own way, and the chemist who correctly stated the question of changes in the elements and of the energy changes accompanying these processes.

BLANK
PAGE

Dear Comrade Editor,

In a number of my papers of the period 1940-1948, when I was concerned with the investigation of the properties and structures of addition products formed between metal salts and unsaturated compounds, I introduced the ideas, concepts, and language of the so-called "theory of resonance" in order to explain the complex chemical behavior of these compounds.

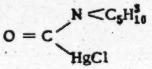
In recent years it has become more and more clear to me that the "theory of resonance and mesomerism" is idealistic, , methodologically invalid, and of no use for investigation purposes.

I came forward with criticism of the "resonance theory" at a number of meetings, in particular at an open session of the Scientific Council of the Institute of Organic Chemistry of the USSR Academy of Sciences, at an open session of the Methodology Seminar of the Chemistry Faculty of the M.V.Lomonosov Moscow State University, and at other places. Later, together with seven other authors, I criticized the idealistic "theory of resonance" in the pages of "Progress in Chemistry", 1950.

I consider it to be my duty to announce in this letter that the concepts of superposition of structures, of ionic and covalent contributions to the state of bonds, and of the hybrid, resonance, or mesomeric structure of molecules, and certain other concepts, introduced into the literature mainly by Pauling and Ingold and, I regret to say, taken up in an uncritical fashion also by me, are unscientific and must be driven out of science.

It follows from what I have said that the explanations that I gave for the pecularities in chemical behavior of compounds such as:

$ClCH = CH - HGCl$[1], $(ClCH = CH)_2Hg$[1],

$ClCH = CHICl_2$[2], 

$O=C(N{<}C_5H_{10})(HgCl)$[3]

are erroneous (they amounted to the assumption of the existence of superimposed structures).

A critical examination of my own work has shown me that the matter of value contained therein is that which is based on A.M.Butlerov's theory – establishment of the structure of compounds of classes indicated above, development of methods for their synthesis, and investigation of their properties from the point of view of the manifestation of the mutual effects of atoms.

LITERATURE CITED

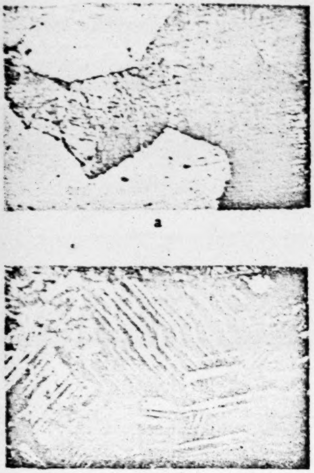
[1] Proc.Acad.Sci.USSR, 26, 59 (1940); Bull.Acad.Sci.USSR, Div.Chem.Sci., 14 (1942), 137 (1945), 657 (1947).

[2] Bull.Acad.Sci.USSR, Div.Chem.Sci., 152 (1943).

[3] Bull.Acad.Sci.USSR, Div.Chem.Sci., 549 (1948).

R. Kh. Freidlina

Mechanical Properties of Alloys of the Magnesium – Cadmium System (page 383).



a

b

Fig. 4. Microstructure of the alloy containing 50 atom-% Cd (X 100). a) Quenched; b) annealed.

Macromolecular Compounds. 2. Significance of the Decarboxylation of Dicarboxylic Acids in the Polycondensation Process (page 509).

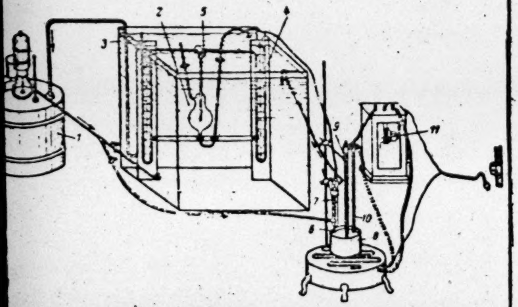


Fig. 1. Diagram of apparatus: 1) thermostat; 2) thermostated vessel of the measuring system; 3) water manometer; 4) mercury manometer; 5) three-way tap for switching from one manometer to the other; 6) tube for decomposition of acid; 7 thermostatic jacket of the reaction tube; 8) bath containing Wood's alloy; 9) contact thermometer for temperature regulation; 10) control thermometer; 11) electromagnetic relay.

The Effect of Alternating Current on the Electrodeposition of Nickel (page 399)

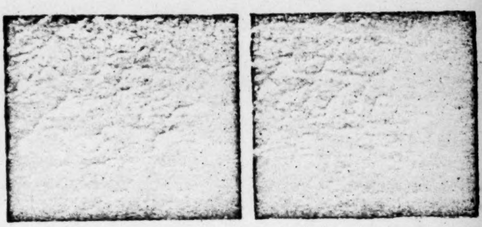


Fig. 2.

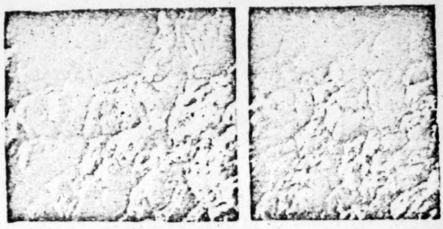


Fig. 3.

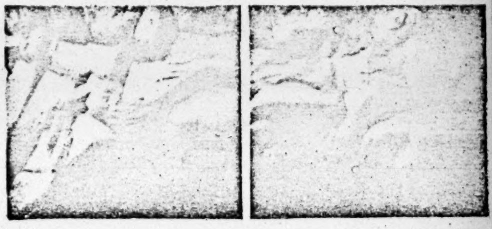


Fig. 4.

BLANK
PAGE

BLANK
PAGE

2 446

55

POROUS STRUCTURE OF ADSORBENTS[*]

M. M. Dubinin

We have during the past few decades witnessed the ever increasing practical application of the phenomenon of adsorption. The most striking examples of technical adsorptional processes realized in the gaseous phase on an industrial scale are the recovery of volatile solvent vapors, the extraction of gasoline from natural gases, and the separation of mixtures of gases. Adsorbents are also widely applied to the purification of liquids and solutions. In all these cases we are concerned with porous adsorbents, which are also of separate interest to industry as carriers of catalysts.

The physical adsorption of gases, vapors, and solutes is basically dependent on the porous structure of adsorbents, which also determines their properties as catalyst carriers. The detailed study of adsorbent structure is hence not only of scientific, but also of considerable practical, interest.

Three kinds of pores are to be found in active charcoals, which are the most widely encountered adsorbents. The biggest are the macropores, which can in many cases be studied with the aid of the optical microscope (Fig. 1). The most suitable method for the detailed study of the distribution of the volumes of macropores according to their effective radii is that depending on the measurement of the volume of mercury, which does not wet the walls of the pores, filling the pores at different hydrostatic pressures. Each pressure $\underline{P}$ has a corresponding effective radius $\underline{r}$, being that of the smallest of the pores filled at that pressure:

$$r = -\frac{2\sigma\cos\Theta}{P}, \tag{1}$$

where σ is the surface tension of mercury, and Θ is the angle of contact of mercury, which we find to be 142°.

A differential curve representing the distribution of pore volumes can be constructed from such measurements, and it is usually characterized by a maximum, corresponding with the prevailing pore diameter. Such maxima on the effective macropore radius distribution curves for various active charcoals fall within the limits 1000 - 10,000 Å. The largest macropores have diameters of the order of thousandths of a centimeter.

The macropores of active charcoals do not affect the values for sorption at equilibrium, and serve only as channels whereby the adsorbed molecules are enabled to penetrate into the interior of the grains of charcoal. The specific surface of the macropores does not exceed 1-2 sq. m. per g., so that the amount of substance adsorbed on their walls is negligibly small.

The transitional pores are smaller in diameter, and become filled with liquid as a result of the process of capillary condensation of vapors of organic liquids adsorbed therein. The non-coincidence of the sorptional and desorptional branches of the isotherms, to give a hysteretic loop, is characteristic of capillary condensation. The volume of the transitional pores is equal to that of vapor (as liquid) sorbed between the equilibrium pressure at which hysteresis is first observed and the saturation value at the relative pressure $\underline{p}/\underline{p}s = 1$ (Fig. 2).

According to the theory of capillary condensation, to each equilibrium vapor pressure there corresponds a definite radius of curvature of the meniscus, which is, under conditions of full wetting, equal to the radius of the free space between adsorption films in the smallest of the filled transitional pores. After introducing a correction for the thickness of the adsorption film we obtain the effective radius of the finest of the filled transitional pores. Such measurements, allowing for the amount of adsorbed vapor, enable us to construct differential curves representing distribution of volumes of transitional pores according to their radius.

The transitional porosity of active charcoals can in most cases also be studied by other methods, such as that of infiltrating mercury under pressure, or by means of the electron microscope (Fig. 3). The effective radii of transitional pores of various active charcoals, corresponding with maxima on the distribution curves, fall within the limits 70-170 Å. Since the volumes of transitional pores of different charcoals vary within broad limits from the order of hundredths to tenths of a cc. per g., it follows that their specific surface may vary from a few square m. to 100 square m. per g.

---

[*] Read at the general meeting of the Division of Chemical Sciences of the Academy of Sciences, U.S.S.R. March 27, 1952.

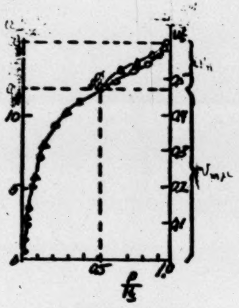


Fig. 2. Sorption and desorption isotherm for methanol vapor at 20°, on active charcoal.

The finest variety of pores are the micropores, which are too small to be seen even with the electron microscope. The study of adsorption from solutions of substances of different molecular sizes, i.e., the application of the method of "molecular sounds" developed by us, allows us to draw the conclusion that the dimensions of the micropores approach those of molecules. Such fine pores or free spaces in the crystalline structure formed by the not fully ordered spatial distribution of the six-membered elementary graphite rings in the turbostratic structure of carbon, give a very considerable specific surface due to micropores of active charcoal, of the order of hundreds of sq. m. per g.

Vapor adsorbed on the walls of micropores is transformed into liquid by the pressure exerted on it. The rapid increase in thickness of the adsorption layer, due to the considerably raised adsorption potential prevailing in the fine micropores, leads to their becoming filled with condensed vapor. The adsorption process is wholly reversible, i.e., the adsorptional and desorptional branches of the isotherms coincide.

In the case of limiting adsorption of sparingly soluble aliphatic acids and alcohols from aqueous solutions the micropores of active charcoal become filled with the pure solute, in the liquid state. The good agreement between the values for the volume of pores filled with condensed vapor at the point of beginning of hysteresis, or with acids or alcohols at limiting adsorption from solutions, served as a basis for the method developed by Kiselev for determination of the volume of the micropores of active charcoal. (For figures 1, 3, and 6, see Plate, page 550-a).

Thus the sorption of organic vapors by active charcoal is made up of an adsorption process leading to the filling up of the micropores, with usually unimportant values of multimolecular adsorption on the surfaces of the transitional pores, and of a process of capillary condensation, which leads to the filling up of the transitional pores. The only exception to this is that of sorption of water vapor, the molecules of which are considerably smaller than are those of organic vapors; the process of adsorption depends only on the relatively weak dispersive forces acting in the presence of the more powerful interaction of dipole water molecules with each other. All this leads to the filling up of the micropores basically as a result of capillary condensation of water vapor. The coarser transitional pores are not as a rule filled in the process of sorption.

As a result there arises the possibility of approximately calculating the distribution of micropore volume according to radii, based on the desorptional branches of the isotherms for water vapor. Such differential distribution curves exhibit a maximum, and give an approximate idea of micropore dimensions. The effective radii of micropores of various active charcoals, corresponding to the maxima of the distribution curves, fall within the limits 11-25Å.

Fig. 4 presents a differential porosity curve for a specimen of charcoal prepared under such conditions as ensure development of all varieties of pores; the numerical data are taken from Aleksandrov, Zaverina, Plachenova, and Chepurniy. The first part of the curve, with a maximum at r = 18 Å corresponds to micropores with a volume of 0.19 cc per g and a specific surface of 240 sq. m. per g. It is derived from the desorptional branch for capillary condensation of water vapor. The second part of the curve, maximum at r = 140 Å, relates to transitional pores, volume 0.49 cc. per g., specific surface ~150 sq. m. per g. Curve 1, Fig. 4, is derived from the desorptional branch for capillary condensation of benzene vapor, without correcting for adsorbed vapor, and Curve 2 is derived from mercury infiltration experiments; the good agreement obtained by different methods for the differential distribution curves for transitional pores is worthy of note. Finally, the third part of the curve, with a maximum at r = 7900 Å, relates to the macropores, volume 0.43 cc. per g., specific surface 1.9 sq. m. per g.

Fig. 5 presents differential distribution curves for volumes of transitional pores according to their radius, instead of its logarithm. Curve 1 is derived from mercury pressure infiltration measurements, Curve 2 from capillary condensation of benzene vapor, measured without correcting for the amount adsorbed, and Curve 3 gives values corrected for the thickness and volume of the adsorption layers. Dzhigit's adsorption isotherm for benzene

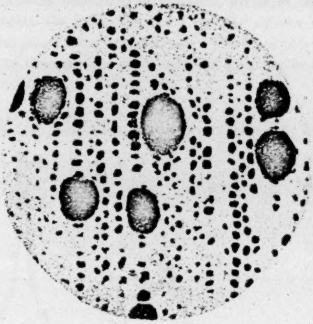


Fig. 1. Photomicrograph of wood charcoal.

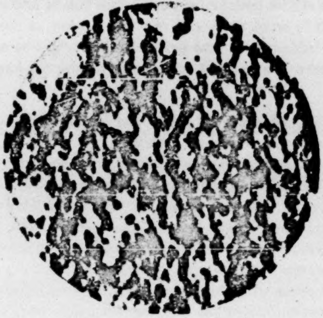


Fig. 6. Electron photomicrograph of silica gel E, shadowed with gold. The pores are seen as dark circles. Magnification 13,000.

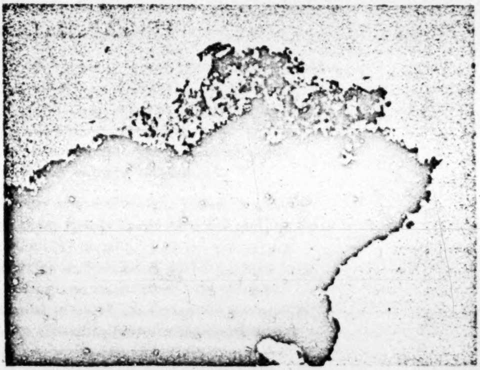


Fig. 3. Electron photomicrograph of sugar charcoal with well developed porosity.

BLANK
PAGE

vapor on lamp black consisting of spherical particles, and activated at 950° in vacuum, was taken for the calculation of the corrections; the adsorbent had a specific surface of 100 sq. m. per g., and from this the volume of the unimolecular adsorption layer was derived. The thickness h of the adsorption film is given for each equilibrium relative pressure by the quotient of the amount of vapor adsorbed and the amount needed for formation of a continuous adsorption monolayer.

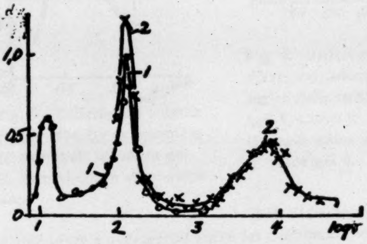


Fig. 4. Differential distribution curves for volumes of all varieties of pores of active charcoal according to logarithms of effective radii.

For each interval of relative pressures along the desorption branch of the isotherm for sorption of benzene vapor by charcoal there corresponded an increment in the volume ΔW_1 of liquified vapor. This increment corresponded approximately to the area of the adsorption film $\Delta s = 2\Delta W_1/R$, which does not differ significantly for such coarse pores from the surface area of the filled pores for the given interval of relative pressures. The product $\Delta sh = w$ gave the volume of the adsorption film. The real volume of the pores ΔW, which is filled within the relevant interval of relative pressures, is expressed by :

$$\Delta W = \Delta W_1 + w - \Delta W_a \qquad (2)$$

where $\Delta W_a = s \cdot \Delta h$ is a correction for the increase in volume of the adsorption film in the larger pores, having a specific surface s, determined by a thermodynamic method. The fraction $\Delta W/\Delta(r + h)$ gave the differential volume of pores, corresponding to an effective radius $r + h$, where r was derived by Thomson's equation for the mean equilibrium relative pressure for the given interval.

The introduction of the correction for adsorbed vapor causes Curve 3 to have a shape similar to that of Curve 1, the position of the maximum being shifted by about 10 Å, being about 6% of the effective radius $r + h$ = 154 Å for the maximum of the curve. This divergence is not a significant one, and the coincidence betweeen curves 1 and 3 may be considered as being satisfactory.

It may thus be said that active charcoals possess in general a tridisperse structure. For many specimens of charcoal the volume of transitional pores is exceedingly small (>0.05 cc. per g), and these charcoals may be regarded as bi-disperse systems, possessing only two kinds of pores: macro- and micro-pores. On the other hand, in specimens of charcoal in which the activation process has been pushed to the limit, the size of micropores increases to that of transitional pores, while macropores becomes still larger than they were. We thus again have a bi-disperse system made up of transitional and macro-pores, with a negligibly small volume of micropores. As has been shown by Kiselev, for such adsorbents the specific surface of the pores s coincides with the specific area of the adsorption film s' at the point at which hysteresis begins. It is obvious that this criterion excludes from consideration the surface of the micropores, if these are present, being fully filled by a purely adsorptional process before capillary condensation commences.

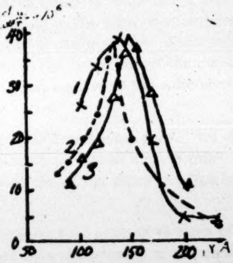


Fig. 5. Differential volume distribution curves for transitional pores of active charcoal according to their effective radii.

A detailed study of silica gels has been made in our laboratory by Kiselev, using a number of specimens specially prepared for the purpose by Neimark. Pore dimensions were determined by the mercury pressure infiltration method by Kiselev and Kamakin.

A peculiarity of the silica gels, connected with the conditions under which they were prepared and in which their structure was formed is the practical absence of pores with diameters corresponding with the macropore class. Thus for the most coarse-pored of the gels studied, silica gel E, the volume of pores of radii exceeding 1000 Å is less than 0.05 cc. per g., as given by the mercury infiltration method. This volume is considerably smaller for the remaining, fine-pored gels.

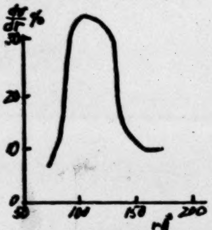


Fig. 7. Differential volume distribution curve according to pore radii for silica gel E, from electron microscope data.

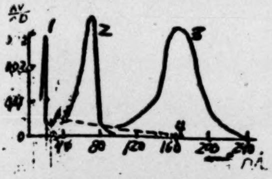


Fig. 8. Differential distribution curves for volume of pores according to their radii. Curve 1: silica gel A, Curve 2: silica gel K, Curve 3: silica gel E, and Curve 4: silica gel B.

Silica gels possess either a uniform pore diameter, and belong in that case to the class of mono-disperse adsorbents, or they have a mixed type of porosity, with a broad gradation of pore diameters. The structure of the relatively coarse-pored silica gels may be observed directly by means of the electron microscope, and it may be studied by the methods of infiltrating mercury under pressure, or of capillary condensation of vapors.

The electron photomicrograph (Fig. 6), prepared by Radushkevich and Lukiyanovich, gives an idea of the uniformly coarse-pored silica gel E, for which the pores may be classified according to their dimensions. A statistical treatment of a large number of such photomicrographs gives a differential curve for distribution of pore volumes according to their radii (Fig. 7). The maximum of this curve corresponds with effective pore radii of about 100 Å, which is in satisfactory agreement with the value derived from the capillary condensation theory.

The sorption measurements give the possibility of constructing more detailed distribution curves, given in Fig. 8, for a number of silica gels. These curves are derived from the theory of capillary condensation from the desorption branches of sorption isotherms of vapors. The abscissas of the graphs represent effective pore diameters in A.

Silica gels 1, 2 and 3 belong to the class of uniform pore size sorbents. Curve 1 relates to the finest pore size silica gel A, most of the pores of which have an effective radius of 15 Å, belonging to the class of micropores. For silica gel K (Curve 2) the maximum of the distribution curve is for pores of effective radius ~40 A. Such pores are close to transitional ones. Finally, for the most coarse-pored silica gel E (Curve 3) the maximum of the curve is at 90 Å, which is typical of transitional pore dimensions. Curve 4 (broken line) gives an idea of the structure of silica gel B with a mixed type of porosity.

We thus see that the pores of silica gels may belong to the classes of micro- and transitional pores. We did not encounter any specimens with well marked bi-disperse structure. There is obviously no reason why, in principle, such silica gels should not exist; such structures have been encountered among the porous glasses studied by Zhdanov.

The experimental data presented in this paper afford confirmation of the conceptions relating to types of pores of adsorbents, as developed by us, in particular for active charcoals, and they show the validity of the methods used for the determination of the volumes of each type of pore, and for their distribution according to pore radius. It should be noted that the terms micropore and macropore are also encountered in the foreign literature, where they are given an arbitrary significance, and express a qualitative picture intended to describe adsorbent structure.

Received April 13, 1952

Institute of Physical Chemistry
Academy of Sciences, U.S.S.R.

NATURAL SORBENTS OF THE FAR EAST. PART 2.

SORPTION OF BENZENE VAPOR BY NATURAL SORBENTS, AND THE STRUCTURE OF SORBENTS

V. T. Bykov

We have for many years conducted a study of natural sorbents (decolorizing earths) with a view to their application in the oil industry for the purification of petroleum products, as well as for purification of products of semicoking of coal, for regeneration of used petroleum lubricants, and for refining of soya bean, seal, and fish oils. These researches demonstrated the effectiveness as decolorizers of earths from a number of locations [1, 2, 3]. In view, however, of the diversity of the requirements of modern industrial practice for sorbents, the time has come to conduct a study of the internal structure of natural sorbents, to classify them according to their structural types, and to achieve a more profound knowledge of their properties, in order to arrive at a fuller and more rational utilization of such solvents in industry.

Natural sorbents are highly disperse bodies with a large internal surface ("specific surface") accessible to vapors and liquids, and attaining an area of the order of hundreds of square meters per gram of sorbent. The conditions under which they were formed, and the factors favoring formation of highly disperse substances in nature, are little known, and they require for their elucidation a systematic study of the properties of such sorbents. Such a study would, moreover, allow the most active ones to be recognized; it is known that certain natural sorbents are in no way inferior to artificially made ones [4].

The investigation of natural sorbents is more difficult than is that of artificial ones, such as charcoals, silica gels, and alumina gels. The natural sorbents are in most cases complex poly-mineral bodies, with diverse particle structures and surfaces. The structure of a natural sorbent plays a very important part in the sorption process. The internal structure of a sorbent is an important factor determining the velocity of sorption, the shape of the isotherm, and the magnitude of adsorption of molecules of the most diverse nature and structure [5, 6]. The geometric structure of an adsorbent, the size of its pores, their distribution according to size, and the heterogeneity of its surface are all factors affecting the magnitude of the adsorption potential. An increase in the adsorption potential, due to summation of attractive fields of opposite walls of the pores, takes place when the radii of the latter are of the same order of magnitude as the field. It is thus necessary, in the study of natural sorbents, to elucidate the structure of the skeleton of the sorbent, and of its pores, to determine the distribution of pore volume according to radius, and to find the nature of the solid – liquid or – vapor interface.

The structure of the skeleton of the sorbent is studied with the aid of the electron microscope and of X-ray analysis. The electron microscope study of natural sorbents allows one to draw conclusions regarding the degree of comminution of the natural product, the shape of its particles, and the mineral nature of the particles (crystals of kaolinite, galluasite, montmorillonite, etc.). The X-ray study of a homogeneous sorbent allows one to draw general conclusions regarding the presence of a given crystalline modification in the sorbent skeleton, to determine the crystalline parameters, and provides evidence concerning the mean degree of dispersion of the skeletal particles. The picture becomes a far more involved one in the case of poly-mineral sorbents, the X-ray analysis of which presents a problem of very great complexity. We have mostly applied the electron microscope method to the study of the skeleton of natural sorbents, as described in a previous paper [15].

We applied very delicate adsorptional methods to the study of pore structure and of distribution of pore volume according to diameter, for typical Far-Eastern natural sorbents. The use of adsorptional methods permitted of a more profound study of the nature of the processes taking place in the pores of a natural sorbent, and gave an insight into its structure.

The complex of measurements necessary in order to reveal the structural type of sorbent, the nature of distribution of pore volume according to radius, the magnitude of the specific surface of the sorbent skeleton, and the area of the adsorption film, has been termed by Kiselev the adsorptional-structural method for the study of highly disperse substances [7, 4]. The study of the structure of a natural sorbent, and of the distribution of the volume of its pores according to radius, is achieved by the use of adsorbates of different molecule size and structure, which penetrate to a greater or lesser amount into the pores, where they undergo adsorption. The development of such adsorptional methods of study of structure may proceed in the following directions, for natural sorbents: (a) study of adsorption of gases and vapors, (b) study of adsorption from solutions, and (c) study of heat of adsorption of vapors and of heat of wetting of sorbents. In addition, various methods for the study of macropores may be applied, such as that depending on their infiltration with liquids under pressure, and on electron microscope observation of the shape and dimensions of particles of the highly disperse substances.

In the study of adsorption of gases and vapors, the small molecules of gas penetrate into the finest pores of the sorbent, and an indication of the magnitude of the internal surface of the adsorbent is given by the amount of gas adsorbed. By determining adsorption of a series of gases and vapors of increasing molecule size an indication of diminishing accessibility of the internal surface is given. However, at saturation the internal surface of adsorbents is not fully covered by gas molecules, since only the active parts of this surface take part in the process, and it is hence preferable to apply the method of sorption of vapors to the study of porous bodies [8]. The results of the application of this method to the study of the structure and properties of natural sorbents are presented in this paper.

The method depending on study of adsorption of dissolved substances also permits one to draw conclusions regarding diminishing accessibility of the adsorbent surface as solute molecule size increases. This method of "molecular probes", supplementing that of sorption of vapors, leads to the characterization of the structure of the adsorbent. The method of adsorption from solutions is more limited in its application than is that of adsorption of vapors, since in the former case complications due to competition between solvent and solute molecules for the adsorbent surface enter. We did not use the methods depending on determination of heats of adsorption of vapors or of wetting of the adsorbent.

Methods Used for Study of the Structure of Natural Sorbents

A vacuum apparatus, with quartz balances, was constructed along the lines of that described by Chmutov [9], with certain modifications, as shown in Fig. 1. The apparatus was designed for the study of the sorbent properties of natural sorbents, by the method of sorption of vapors, in the Sorption Processes Laboratory, Institute of Physical Chemistry, Academy of Sciences, U.S.S.R.

The vacuum apparatus possesses four sorption tubes 1, within which are suspended calibrated quartz spirals 2, from hooks forming part of the ground glass stoppers, which are used without grease, being sealed with mercury. The cups 3 containing weighed amounts of natural sorbent were suspended by glass threads from the quartz spirals. The sorption tubes were connected with two MacLeod mercury manometers 4 and 5, covering the range 8.67×10^{-6} to 7.44×10^{-1} mm., and with a U-shaped mercury manometer 6, permitting, with the aid of a cathetometer with a reading microscope, of the measurement of vapor pressure, up to saturation, and then with a Bauer valve for the introduction of vapor 7, with an applicator tube 8. The instrument is then connected through a U-shaped safety tube 10 through tap 11 to a Langmuir mercury diffusional three-stage pump 12, with a pre-vacuum system.

The measurements are made as follows: portions of 70-100 mg of air-dry or dried natural sorbents are weighed out in weighed cups. In most cases the sorbents were powdered and passed through a sieve with 6400 apertures per sq. cm. The cups, containing portions of natural and standard sorbents, are suspended in the sorption

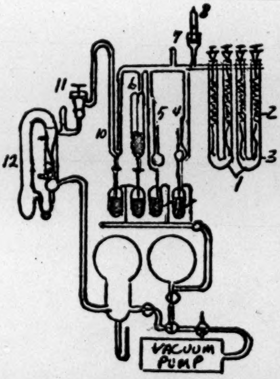


Fig. 1. Vacuum apparatus for study of sorption.

tubes, and the mercury seals are applied to the cocks. The initial position of an indicator on the glass threads is read with the aid of a cathetometer fitted with a microscope, on a scale placed within the sorption tubes.

An electric heater is placed under the sorption tubes, and air is pumped out, at first using the low-vacuum pump, and then the mercury diffusion pump 12, with the lower part of the sorption tubes at 200°. Evacuation is continued until the pressure falls to 10^{-5} mm. Tap 11 is then closed, and heating is discontinued; the heater is removed during the cooling process, and the position of indicators on the glass threads is read on fixed scales within the tubes.

The loss of weight of the sorbents indicates removal of moisture and gases. Further calculations are now based on the dry weight of the sorbents. The lower parts of the tubes are now immersed in a water thermostat at 20° (this was taken as the standard temperature for all our measurements). A small amount of vapor is now introduced into the system, by contacting for a short time the porous membrane of applicator tube 8 (containing degassed liquids, such as benzene, methanol, etc.) with a porous diaphragm of funnel 7. Slight elevation of the tube 8 allows a layer of mercury to separate the membranes, so preventing further diffusion of vapor into the vacuum system.

After establishment of equilibrium, as shown by cessation of movement of the pointers on the glass threads and by achievement of constant pressure, the displacement of the pointers is read off on the scales, which are graduated in 0.01 mm. The equilibrium vapor pressures are read on the MacLeod manometers 4 and 5 and the mercury manometer 6, with the aid of a cathetometer. A fresh portion of vapor is then introduced, and readings are again taken after establishment of the new equilibrium. These manipulations are continued until full saturation of the sorbent is achieved. The lower part of the U-shaped safety tube 10 is filled with mercury in order to protect the grease of tap 11 from the action of the vapors.

The desorptional branch of the isotherm is obtained by measuring equilibrium pressure and loss of weight of sorbent following progressive lowering of pressure obtained by opening tap 11 so as to connect with the low vacuum system. The establishment of equilibrium during desorption takes place very slowly; several days may be needed to obtain one point on the isotherm. The sorption and desorption isotherm measurements were usually repeated 2-3 times, from a high vacuum to full saturation, and back again. In addition to this, control measurements were made, involving comparison with standard sorbents. In order to increase the accuracy of the measurements the whole apparatus was placed in an air thermostat, in addition to keeping the lower parts of the sorption tubes in a water thermostat.

We initially took measurements of sorption of methanol vapor, but the majority of natural sorbents exhibit swelling of the skeleton and show that a chemosorptive process has taken place [7]. We therefore abandoned work with methanol, and concentrated on measurement of sorption of benzene vapor. The work of the sorption apparatus was checked by reference to a standard sorbent AG(II), for which trustworthy adsorption isotherms for benzene vapor had been derived in Dubinin's laboratory.

Checking and calibration of the quartz spirals were systematically performed during the course of the experiments.

Experimental Data on Sorption and Desorption of Benzene Vapor by Natural Sorbents

Two or more samples of each natural sorbent were taken from each of the more important deposits, preferably from those parts which were under exploitation or were suitable for exploitation. The degree of weathering of the tuffs from each particular location varies to some extent within it, and the sorptive properties will obviously also vary accordingly. It was for this reason desirable to take samples of the actual product being dug up and transported from the site.

Sorption and desorption isotherms for benzene vapor were derived for samples of ashy liparite tuffs and their weathering products. These minerals are of noegene origin, and they belong to the so-called Suyfun deposite [10]. They are represented in this paper by samples No. 17, 18, 19, and 135 (ashy tuffs), and Nos. 20, 124, 127, and 130 (weathered ashy tuffs).

Many of the natural sorbents studied were products of weathering of agglomerative tuffs from early quaternary volcanoes [11, 12]; the samples studied were Nos. 91, 92, 93, 86, 87, 88, 95 and 96. In addition we studied the diatomaceous earths Nos. 81, 82, 99, 101, and 142. In order to compare the properties of the basic group of Far Eastern natural adsorbents with their more important counterparts from the European U.S.S.R. we obtained the

Sorption and desorption isotherms for benzene vapor on gumbrine, Nalchkine and Fuller's earth, at 20°

Table 1 gives the volumes of sorbed benzene in cubic centimeters per gram of sorbent for different degrees of saturation and presents values for the specific surface of the sorbent skeleton and for the area of the adsorption film. The determination of the specific surface of the sorbent skeleton was performed by the method of Brunauer, Emmett and Teller [13] and of the area of the adsorption film by Kiselev's method [14].

TABLE 1
Sorption of Benzene Vapor by Natural Sorbents

Description of samples and specimens	No	Point of beginning hysteresis	Volume of sorbed benzene in cc/g × 10					Specific surface	
			At the point of beginning of hysteresis	At p/p_s 0.25	At p/p_s 0.5	At p/p_s 0.95	At full saturation	Of the skeleton S in m/g	Of the adsorption film S' in m/g
Ashy tuff	17	0.15	13	18	32	81	141	26	19
	18	0.15	18	27	37	80	136	40	27
	135	0.20	18	22	41	100	147	34	29
Weathered tuff	20	0.15	14	27	46	90	102	(27)	39
	124	0.17	18	34	58	119	143	40	(49)
	130	0.16	17	35	58	123	147	38	(35)
Agglomerative tuffs	84	0.50	9	8	9	55	88	14	8
Intact	170	0.34	11	10	14	26	29	12	–
	122	0.18	38	48	95	202	295	77	77
Weathered	173	0.30	44	39	65	155	290	76	–
"	123	0.15	14	20	39	169	309	(32)	48
	96	0.16	25	36	54	121	220	46	40
	95	0.15	31	55	75	131	162	57	49
	91	0.18	40	51	82	1[illegible]4	139	76	51
	92	0.15	16	32	51	88	222	42	–
	93	–	–	31	61	178	248	82	–
"	86	0.14	41	76	118	208	212	85	83
	87	0.18	25	38	59	214	369	40	53
	88	0.20	99	112	169	700	844	195	132
	94	0.20	76	87	167	688	866	154	150
Diatomaceous earths	81	(0.32)	(19)	18	31	82	323	26	14
"	82	(0.33)	(24)	–	–	–	373	33	18
"	99	0.18	17	21	31	82	125	33	8
"	101	0.14	18	30	42	86	179	34	29
"	142	0.23	18	19	27	104	176	29	16
Industrial bleaching earths:									
Fuller's earth	30	0.175	46	55	105	309	446	88	(96)
Activated gumbrine	71	0.175	36	56	102	206	223	68	72
Nalchkine "B"	74	0.18	32	35	54	430	503	53	(69)
Nalchkine "C"	73	0.17	54	66	97	182	208	87	52
[illegible]yab	75	0.27	53	50	93	130	149	83	34

All the sorption isotherms obtained for natural sorbents are S-shaped, as can be seen in Figs. 2-9, in which the ordinates represent amounts of sorbed (rings) or desorbed (circles) benzene vapor, in millimoles per gram of sorbent, while the abscissas are equilibrium relative pressures. An analysis of the sorption isotherms suggests a relatively inconsiderable adsorption of benzene vapor by ashy liparite tuffs (samples No. 17, 18 and 19), rising for medium saturation for weathered tuffs (Nos. 20, 124 and 130), as appears from the Table and from Figs. 3 and 4. The specific surface of ashy tuffs varies from 25 to 35 m/g, and for weathered ashy tuffs from 30 to 40 m/g.

Weathered agglomerative tuffs have much greater sorbent power. The original volcanic agglomerative tuffs in their intact unweathered state (samples No. 84 and 171) gave only small sorption values, amounting at saturation to 0.088 0.062 cc/g, and they had small specific surface values of 14 12 sq. m per g. The products of weathering of agglomerative tuffs have good adsorbent properties, with elevated values for adsorption at low and medium saturations, and with the amount of benzene sorbed at full saturation 2-3 times greater. The specific surface is 5-6 times greater, attaining values of 70-90 sq. m. per g. The separate inclusions of argillaceous minerals formed during weathering of agglomerative tuffs have a high adsorbent activity. Thus, for example, sample No. 88 (magnesial montmorillonite from inclusions in agglomerative tuff) gives a limiting sorption of benzene equal to 0.844 cc./g., and has a specific surface equal to 195 sq. m. per g., i.e., its adsorptive properties exceed those of some artificial adsorbents. Similar high activity is shown by montmorillonite from another location (sample No. 94).

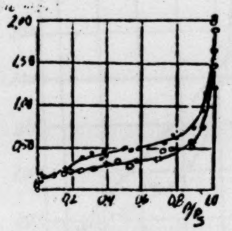


Fig. 2. Sorption and desorption isotherm for benzene vapor on ashy tuff (sample No. 18).

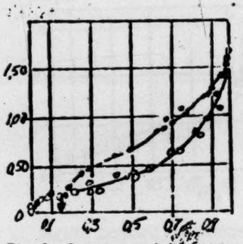


Fig. 3. Sorption and desorption isotherm for benzene vapor on weathered ashy tuff (sample No. 130).

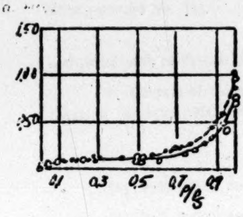


Fig. 4. Sorption and desorption isotherm for benzene vapor on agglomerative tuff (intact, sample No. 84)

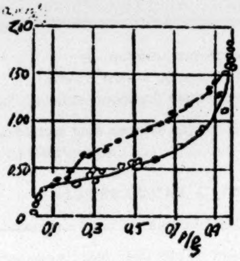


Fig. 5. Sorption and desorption isotherm for benzene vapor on agglomerative weathered tuff (sample No. 95).

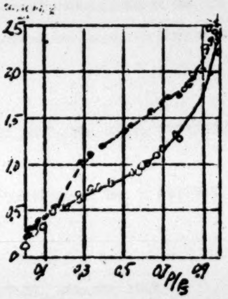


Fig. 6. Sorption and desorption isotherm for benzene vapor on agglomerative weathered tuff (sample No. 86).

A number of samples of diatomaceous earths (samples No. 99, 101 and 142) exhibit sorbent properties of the same order as liparite ashy tuffs and their weathering products. However, samples of diatomaceous earth from one location (Nos. 81 and 82) had a very high sorptive capacity attributable to capillary condensation at high degrees of saturation, which is evidence of the relatively coarse pores of these samples. These sorbents should therefore be suitable for purification of heavy petroleum products from which large molecule size admixtures are to be removed.

The active natural sorbents studied by us for purposes of comparison, and which include the most important bleaching earths of the U.S.S.R., are characterized by the steep rise in the isotherm at the point of beginning of hysteresis, where adsorption amounts to 0.4-0.6 mM/g., or 0.030-0.050 cc./g., with a considerable part of the sorption being due to capillary condensation, leading at saturation to sorption of 0.20-0.50 cc./g. All the highly active natural sorbents are characterized by a diffuse distribution of pore volume according to radius, with a considerable fraction of coarse pores.

The comparison of these with the Far Eastern sorbents shows that the isotherms for a series of agglomerative weathered tuffs are close to and similar to those for gumbrine, Gilyabi, and Fuller's earth. This similarity of isotherms reflects a similarity of structures of these natural sorbents, and suggests that they have similar adsorptive properties. The agglomerative tuffs in many cases exhibit high sorptive activity, and they should be useful as bleaching earths for mineral and vegetable oils.

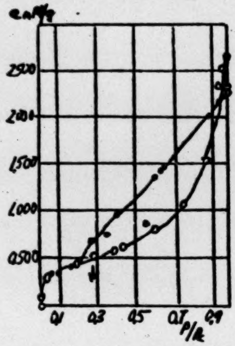


Fig. 7. Sorption and desorption isotherm for benzene on activated gumbrine (sample No. 71).

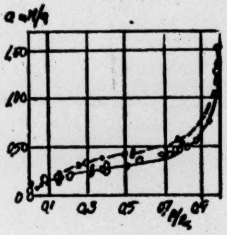


Fig. 8. Sorption and desorption isotherm: for benzene vapor on diatomaceous earth (sample No. 101).

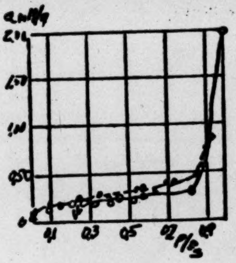


Fig. 9. Sorption and desorption for benzene vapor on diatomaceous earth (sample No. 142).

SUMMARY

1. Sorption and desportion isotherms for benzene vapor on natural sorbents from a number of deposits have been constructed, and have been compared with isotherms for some of the more important natural sorbents taken from European parts of the U.S.S.R.

2. Certain of the sorbents exhibited high sorptive capacity, and had structures and properties similar to those of gumbrine, Nalchikines, and Fuller's earth.

LITERATURE CITED

[1] V.T. Bykov and V.I. Alekseeva, Bull. Far Eastern Filial Acad. Sci., U.S.S.R., No. 33 (1), 107 (1939).

[2] V.T. Bykov and V.I. Alekseeva, ibid., No. 33 (1), 116 (1939).

[3] V.T. Bykov, Publications Far Eastern Base Acad. Sci. U.S.S.R., Chemical Series, No. 1, 59 (1947).

[4] A.V. Kiselev, Bull. Moscow State Univ., 11, 111 (1949).

[5] M.M. Dubinin, Physico-Chemical Principles of Sorption Technique, State Sci. Tech. Press, 1935.

[6] S. Brunauer, Adsorption of gases and vapors. 1. Foreign Literature Publ., Moscow, 1948.

[7] A.V. Kiselev, Thesis, Moscow State Univ. 1950.

[8] M.M. Dubinin, Problems of kinetics and catalysis, 5, 123 (1948).

[9] M.M. Dubinin and K. Chmutov, Physico-Chemical Principles of anti-Gas Measures. Mil. Chem. Acad. Publ. Moscow, 1939.

[10] E.F. Maleev, Bull. Far Eastern Filial Acad. Sci. U.S.S.R., 28 (1), 37 (1938).

[11] E.F. Maleev, Soviet Geology, No. 12, 45 (1945).

[12] E.F. Maleev, Publications Vulcanology Lab. Acad. Sci. U.S.S.R., 6, 23 (1949).

[13] S. Brunauer, P. Emmett, and E. Teller, J. Amer. Chem. Soc., 60, 309 (1938).

[14] A.V. Kiselev and N.A. Mikos, J. Phys. Chem., 22, 1043 (1948).

[15] V.T. Bykov, V.M. Lukiyanovich, and L.V. Radushkevich, Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci., No. 3, 406 (1952). (See Consultants Bureau translation, page 395.)

Received November 5, 1951

Laboratory of Sorptional Process
Institute of Physical Chemistry
Academy of Sciences, U.S.S.R.

ROLE OF INERT DILUENTS ON CATALYTIC DEHYDROGENATION OF ETHYLBENZENE

N. I. Shuikin and I. I. Levitsky

Numerous papers on catalytic dehydrogenation of ethylbenzene to give styrene have been published during the past decade. A well known method of raising the styrene content of the catalyzates depends on dilution of the ethylbenzene with inert gases (CO_2, N_2, steam) [1,2]. This effect is explained [1,3,4] as being due to lowering of the velocity of the side reaction of cracking and polymerization of styrene, due to lowering of the concentration of the latter in the vapor phase.

The method of kinetic determination of relative adsorption coefficients was applied in one of the papers cited [4] to the study of the effect of carbon dioxide on the dehydrogenation of ethylbenzene. It was found that the styrene content of the catalyzates rose from 33 to 56.3% as the carbon dioxide content of the reaction mixture rose from 0 to 88%. The author comes to the conclusion that the adsorption coefficient of carbon dioxide is equal to zero, and that the depth of dehydrogenation of ethylbenzene remains constant, and is not affected by dilution with carbon dioxide. The increased yields of styrene are ascribed to inhibition of polymerization; no numerical data in support of these views are presented, however.

Marukyan [5] and Tolstopyatova [6] found that depth of dehydrogenation of ethylbenzene rises as it is diluted with xylenes, toluene, or benzene, and falls with increasing styrene content. The authors ascribe these effects to the circumstance that the adsorption coefficients of xylenes, toluene, and benzene are considerably lower, and of styrene higher, than is that of ethylbenzene. These results, moreover, led to the derivation of "a generalized kinetic equation for catalytic unimolecular reactions at homogeneous surfaces in a flowing system, allowing for displacement by other substances present" [6]. The role of inert gases and hydrocarbons is thus believed by the above authors to be due exclusively to kinetic factors.

The role of inert diluents may, however, be of an entirely different nature, if the reaction of dehydrogenation of ethylbenzene has under the given conditions been able to approach or reach a state of thermodynamic equilibrium:

$$C_6H_5{-}CH_2{-}CH_3 \rightleftharpoons CH{-}C_6H_5{=}CH_2 + H_2.$$

This reaction proceeds with increase in volume, for which reason inert diluents should, in the same way as lower pressures, cause lowering of the partial pressures of the components of the equilibrium mixture, and hence shift the equilibrium in the direction of styrene production.

Mitchell [7] has already expressed a similar opinion on the role of steam in the dehydrogenation of ethylbenzene, without, however, advancing any experimental or numerical data in support of it.

The object of the research described in this paper was to find how close the product of dehydrogenation of ethylbenzene over catalysts of ordinary activity is to the composition of the thermodynamic equilibrium mixture, and to find whether addition of inert diluents shifts the equilibrium towards higher styrene production.

EXPERIMENTAL

Research Methods

Apparatus. The reactor was a quartz tube of internal diameter 20 mm placed in an electric oven 90 cm long, which maintained a uniform constant temperature over a length of 40 cm. The supply of current to the oven was controlled by a thermo-regulator with a mercury relay, the fluctuations in temperature not exceeding ± 1°. Temperatures were measured by a compensational method, using a chromium-aluminum thermocouple, which was carefully calibrated. The thermocouple was placed within a porcelain sleeve situated in the middle of the catalyst layer. The reaction tube was connected with a three way tube, serving for introduction of ethylbenzene from an automatic burette, of the diluent, and of the thermocouple leads. The distal end of the tube was connected with a receiver cooled in ice.

The catalyst, containing vanadium oxide, differed very little in stability and activity from Marukyan's [8] copper-chromium catalyst. All the experiments described were performed with a single specimen of catalyst, with a volume of 50 ml.

Analysis. The styrene content of the catalyzates was determined by bromometric titration by Rosenmund's method [9]. The analyses were performed immediately after each experiment, since the styrene content changes significantly when the catalyzates are stored.

Performance of the experiments. The catalyst was regenerated after each experiment by passing through it a current of air at 575-600° for 90 minutes. The initial activity of the catalyst was thus maintained throughout our experiments. After regeneration the reaction tube was swept out with a stream of nitrogen or carbon dioxide, after which we began the introduction of a stream of the gas (nitrogen or hydrogen) in presence of which the given experiment on dehydrogenation of ethylbenzene was being conducted; the flow of gas was regulated by means of a rheometer. All experiments were conducted at 575°, the temperature being raised initially to about 585°, so that the actual dehydrogenation took place at 574-576°. Four to eight ml of ethylbenzene were then introduced, at an appropriate rate, and the experiment was commenced when conditions had become stabilized, when the receiver was changed. A total of 8-15 ml of ethylbenzene or of its mixtures with toluene was passed through the tube.

Substrates. The ethylbenzene, after being boiled over sodium, had the following constants: b.p. 135.9-136.1°, n_D^{20} 1,4966, d_4^{20} 0.8664. The toluene was distilled from sodium; it had b.p. 110.5-111.0°, n_D^{20} 1,4960, and d_4^{20} 0.8662. The nitrogen used as a diluent was first passed through a red-hot quartz tube containing freshly reduced copper, and then through a calcium chloride tube and a rheometer, before entering the reaction tube. Hydrogen was first passed through a tube containing platinized charcoal, then over calcium chloride, and then through a flow meter to the reaction tube.

Dehydrogenation of Undiluted Ethylbenzene

Dehydrogenation in absence of diluents was studied at different molar flow velocities, given in the Tables as moles of substance passed per hour through 1 liter of catalyst; the corresponding volume velocities are expressed as liters per hour per liter of catalyst.

TABLE 1

Dehydrogenation of Ethylbenzene without Diluents

No. of Experiment	Volume velocity	Molar velocity	Yield of catalyzate, as % of ethylbenzene passed	Styrene content of the catalyzate, as % by weight
1	2	3	4	5
2	0.30	2.4	88	18.6
3	0.63	5.2	91	23.1
4	1.04	8.6	94	24.8
5	1.20	9.9	94	25.4
7	1.47	12.1	95	26.3
34	1.77	14.6	96	24.3
6	1.91	16.0	97	25.4
35	2.40	19.8	94	24.7

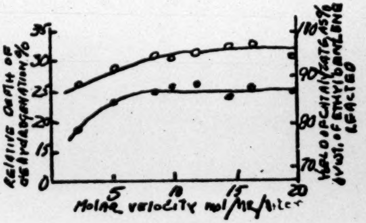


Fig. 1. Dehydrogenation of ethylbenzene without diluents: ● = relative % dehydrogenation; O = yield of catalyzate.

A rise in the molar velocity of ethylbenzene from 2.4 to 8.6 leads to a rise in the styrene content of the catalyzate, from 18.6 to 24.8%. It may be supposed that polymerization of the styrene produced varies parallel with duration of contact with the catalyst. This explanation is confirmed by a corresponding increase in the yield of catalyzate from 88 to 94%.

Further increase in molar velocity from 8.6 to 19.8 has no further effect on the yields of catalyzate, or on its styrene content. This constancy of the relative depth of dehydrogenation of ethylbenzene, and its independence of duration of contact may be due to the reaction attaining thermodynamic equilibrium. The independence of the yields of catalyzates and of the relative depths of dehydrogenation (taken as being equal to the styrene content of the catalyzates) of molar velocity is illustrated by the curves of Fig. 1.

The constant depth of dehydrogenation of ethylbenzene at different molar velocities has already been reported by other workers. Marukyan [8] obtained the same yields of styrene from 1:2 ethylbenzene vapor-carbon dioxide mixtures at 600°, when the molar velocity was varied from 8.2 to 22.4. It may be supposed that side-reactions could not significantly affect the constancy of the depth of dehydrogenation. The pyrolysis of ethylbenzene and styrene, and the polymerization of the latter have been studied by Marukyan and Tolstopyatova [10] for flowing systems; they found that variations in duration of contact did not cause any considerable change in the extent to which these reactions proceeded. Thus at 575°, with a time of contact of 155 sec. 5.9% of the styrene was decomposed, as compared with 3.0% for 77 or 31 sec.

It is quite obvious that the actual depth of dehydrogenation of ethylbenzene was somewhat more than the values found by us. The temperature of our experiments was such as would involve the reactions of cracking and polymerization. The depth of dehydrogenation at equilibrium calculated by us from free energy and heat content functions was found to be 34% at 575°, which exceeds the experimental value by about 9%. This difference is somewhat greater than the value for losses (cf. Column 4, Table 1) due chiefly to polymerization of styrene.

Dehydrogenation of ethylbenzene mixed with hydrogen, nitrogen, or toluene was studied at molar velocities of 8.6-19.6. It was of interest to compare the experimental results with those derived from thermodynamic calculations based on our experimental results, instead of on the values given by spectrum analysis. Agreement between calculated and experimental results would be decisive evidence in favor of the existence of a dynamic equilibrium. For the calculation of the equilibrium constants of the reaction we took the value of 25% for the relative equilibrium depth of dehydrogenation of ethylbenzene in the absence of a diluent; this value is the mean of those obtained in experiments 4-7, 34, and 35 (Table 1).

The thermodynamic calculations of all the experiments of this research were made with the aid of the well known equation [11] (compare with [12]), which for the reaction

$$bB + cC = rR + sS$$

has the form

$$K_p = K_n\left(\frac{P}{n_B + n_C + n_R + n_S + n_{in}}\right)^{(r+s)-(b+c)} \qquad (1)$$

Here

$$K_p = \frac{p^r_R p^s_S}{p^b_B p^c_C},$$

where $P_{R,S\ldots i}$ is the partial pressure of the i-th reacting component, $n_{R,S\ldots i}$ is the number of moles of the i-th component in the equilibrium mixture, n_{in} is the number of moles of inert diluent present in the equilibrium mixture, $K_n = \frac{n^r_R n^s_S}{n^b_B n^c_C}$, and P is the external pressure.

For the reaction $\underset{1}{C_6H_5{-}CH_2{-}CH_3} = \underset{2}{C_6H_5{-}CH = CH_2} + \underset{3}{H_2}$, conducted at atmospheric pressure without dilution, and for dehydrogenation of 1 mole of ethylbenzene with production of x moles of styrene the separate terms of equation (1) will be equal to: $n_1 = 1-x$;

$$n_2 = n_3 = x;\ P = 1;\ n_{in} = 0;\ (r+s)-(b+c) = 2-1 = 1.$$

Substitution of these values in equation (1) gives:

$$K_p = \frac{n_2 n_3}{n_1(n_1 + n_2 + n_3)} = \frac{x^2}{(1-x)(1+x)} = \frac{x^2}{1-x^2} \qquad (2)$$

The depth of dehydrogenation at equilibrium was taken as 25.0%, whence x = 0.25, the substitution of which in equation (2) gives $K_p = 0.0667$. All further thermodynamic calculations were based on the value of K_p so found.

Dehydrogenation of Ethylbenzene Vapor Diluted with Hydrogen

Addition of hydrogen should shift equilibrium in the direction of diminution of dehydrogenation, and should lead to a lowering of the styrene content of the catalyzates. Percentage conversion of ethylbenzene into styrene will then be determined by the degree of dilution with hydrogen. The depth of dehydrogenation calculated on the basis of the above-derived equilibrium constant should coincide with the experimental values under two conditions: (a) the reaction actually attains equilibrium, and (b) the depth of the side reactions of polymerization and cracking remains constant whether or not a diluent is used. In this series of experiments we wished to elucidate the effect of dilution with hydrogen on dehydrogenation of ethylbenzene, and to ascertain whether the calculated results coincide with the experimentally found ones.

In the dehydrogenation of 1 mole of ethylbenzene, with production of $\underline{x}$ moles of styrene, and with dilution of each mole of ethylbenzene with $\underline{m}$ moles of hydrogen, the equilibrium mixture will have the composition: $n_1 = 1-x$; $n_2 = x$; $n_3 = x + m$. Substituting these expressions in the left-hand side of equation (2) we obtain:

$$K_p = \frac{n_2 n_3}{n_1(n_1 + n_2 + n_3)} = \frac{x(x + m)}{(1-x)(1 + x + m)}$$

which after simple transformations gives

$$(1 + K_p)x^2 + (m + Kpm)x - Kp(1 + m) = 0 \qquad (3)$$

The results of all the experiments of this series are calculated from equation (3). The degree of dilution of ethylbenzene with hydrogen, m, was determined by dividing the molar velocity of hydrogen by that of ethylbenzene.

The results obtained are presented in Table 2 and the values of columns 11 and 12 are shown in the graph of Fig. 2 (lower curve). The styrene content of the catalyzates fall with increasing dilution from 23.2 to 10.2%. For all ethylbenzene-hydrogen ratios studied the calculated values were 3.0-4.5% lower than the experimental ones; the deviations are shown in the last column of Table 2. These deviations could be predicted, as being a result of inhibition of the reaction of polymerization of styrene, with consequent raising of the yield of the latter. However, the small and practically constant value of the deviations suggests that the reactions had attained equilibrium.

The yields of catalyzate obtained, as percentage of ethylbenzene introduced *, are somewhat higher than found for experiments without diluent (compare column 10, Table 2 with column 4, Table 1); this testifies to lowering of depth of side reactions in systems diluted with hydrogen.

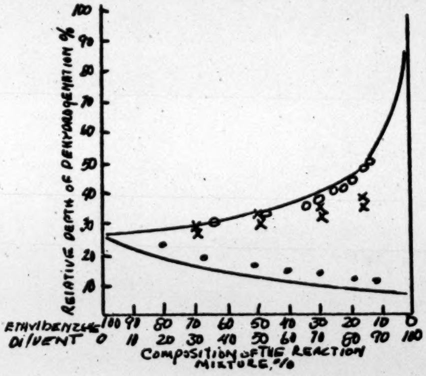


Fig. 2. Dehydrogenation of ethylbenzene diluted with hydrogen, nitrogen and toluene: lower curve - calculated from equation (3) for hydrogen; upper curve - calculated from equation (4) for inert diluents (o - for nitrogen, x - for toluene, ● - for hydrogen).

Dehydrogenation of Ethylbenzene Vapor Diluted with Nitrogen

We next investigated whether dilution with nitrogen was analogous to conducting the reaction at reduced pressure. Given degrees of dilution with nitrogen should, similarly to given reductions in pressure, lead to the obtaining of yields of styrene such as could be calculated from equation (1). Should calculated and experimental results be in agreement this would afford additional evidence of the attainment of an equilibrium state.

In the dehydrogenation of 1 mole of ethylbenzene with production of 1 mole of styrene, the ethylbenzene

---

* This refers to the amount of ethylbenzene passed over the catalyst during the experiment.

TABLE 2

Dehydrogenation of Ethylbenzene Vapor Diluted with Hydrogen

No.	Volume velocity of ethylbenzene	Velocity of hydrogen in l/hr (NTP)	Molar velocity			Molar composition of the mixtures, %		Degree of dilution m	Yield of catalyzate as % of ethylbenzene introduced	Depth of dehydrogenation, %		Deviation
			Ethylbenzene	Hydrogen	Total	Ethylbenzene	Hydrogen			Styrene content of catalyzate	Calculated from eq.(3)	
1	2	3	4	5	6	7	8	9	10	11	12	13
29	1.24	2.8	10.2	2.5	12.7	80.3	10.7	0.25	96	23.2	19.6	+3.6
30	1.21	5.5	10.0	4.9	14.9	67.2	32.8	0.49	97	18.7	14.7	+4.0
31	0.92	8.2	7.6	7.3	14.9	51.0	49.0	0.96	97	16.0	11.5	+4.5
32	0.60	8.2	4.9	7.3	12.2	40.0	60.0	1.5	96	14.6	9.8	+4.6
33	0.64	13.8	5.3	12.3	17.6	30.0	70.0	2.3	97	12.7	8.6	+4.1
28	0.32	13.8	2.7	12.3	15.0	17.8	82.2	4.6	93	11.5	7.5	+4.0
27	0.17	13.8	1.4	12.3	13.7	10.5	89.5	8.5	93	10.2	7.1	+3.1

being initially diluted with n_{in} moles of nitrogen (or other inert diluent) per mole of ethylbenzene, the mixture of components of the equilibrium mixture with diluent will have the composition (see above): $n_1 = (1 - x)$; $n_2 = n_3 = x$ and n_{in}. Substituting these expressions into equation (1), and on condition that P = 1, we obtain:

$$K_p = \frac{n_2 n_3}{n_1(n_1 + n_2 + n_3 + n_{in})} = \frac{x^2}{(1 - x)(1 + x + n_{in})}.$$

A series of simple transformations of this equation leads to

$$(K_p + 1)x^2 + K_p n_{in} x - K_p(n_{in} + 1) = 0 \tag{4}$$

All further calculations are made by substituting in equation (4). The dilution n_{in} was derived by dividing the molar velocity of nitrogen by that of ethylbenzene.

TABLE 3

Dehydrogenation of Ethylbenzene Vapor Diluted with Nitrogen

No.	Volume velocity of ethylbenzene	Velocity of nitrogen in l/hr (NTP)	Molar velocity			Molar composition of the initial mixture, %		Degree of dilution n_{in}	Yield of catalyzate as % of ethylbenzene introduced	Depth of dehydrogenation, %		Deviation %
			Ethylbenzene	Nitrogen	Total	Ethylbenzene	Nitrogen			Styrene content of catalyzate	Calculated from eq.(4)	
1	2	3	4	5	6	7	8	9	10	11	12	13
24	1.04	5.2	8.6	4.7	13.3	64.6	35.4	0.55	91	29.5	29.5	0
23	0.98	9.6	8.1	8.6	16.7	48.5	51.5	1.1	87	32.2	32.9	−0.7
16	0.41	7.6	3.4	6.8	10.2	33.5	66.5	2.0	87	36.4	37.5	−1.1
22	0.68	14.0	5.6	12.5	18.1	30.9	69.1	2.2	79	37.1	38.4	−1.3
18	0.50	14.0	4.1	12.5	16.6	24.7	75.3	3.0	75	41.7	41.6	+0.1
21	0.48	14.0	4.0	12.5	16.5	24.2	75.8	3.1	74	41.7	41.9	−0.2
20	0.39	14.0	3.2	12.5	15.7	20.4	79.6	3.9	71	43.3	44.4	−1.1
26	0.28	14.0	2.4	12.5	14.9	16.1	83.9	5.3	67	48.1	48.3	−0.2
19	0.24	14.0	2.0	12.5	14.5	13.8	86.2	6.2	65	49.5	50.4	−0.9

The results are given in Table 3, the values of Columns 11 and 12 being taken for the upper curve of Fig. 2. The difference between calculated and experimental values for depth of dehydrogenation does not exceed 1.3% (last column). This good agreement is strong evidence that the reaction has attained a state of thermodynamic equilibrium. The increased yields of styrene obtained when the ethylbenzene is diluted with inert gases (nitrogen, carbon dioxide, steam) are therefore ascribable to displacement of the equilibrium point in the direction of greater dehydrogenation, and not to the decreased velocity of side reactions.

It is of interest that the differences between calculated and experimental values are greater with hydrogen (3.0-4.5%) than with nitrogen (up to 1.3%). The depth of the reaction of polymerization of styrene is smaller in presence of hydrogen than in absence of a diluent, and this is ascribable to two factors: the fall in the yields of styrene, and its dilution with hydrogen. These factors act in opposite directions when the diluent is nitrogen; increase in the yields of styrene raises the velocity of the polyemnization reaction, while dilution with nitrogen reduces it. As a result, the depth of polymerization of styrene is practically the same with nitrogen as a diluent as without diluent.

The figures of Column 10, Table 3, are of interest. They show that the yield of catalyzate falls from 91 to 65% as dilution with nitrogen increases, whereas comparable dilutions with hydrogen gave consistently high and practically constant yields (93-97%). This effect may be connected with the high thermal conductivity of hydrogen, which is 7 times greater than that of nitrogen [13]. Under conditions in which ethylbenzene and styrene would have had time to condense from a hydrogen atmosphere, a stream of nitrogen would have carried some of the catalyzate from the receiver.

Dehydrogenation of Ethylbenzene - Toluene Mixtures

It was remarked in the introduction to this paper that the rise in depth of dehydrogenation of ethylbenzene due to dilution with toluene has been explained [6] as being a consequence of differences between adsorption of ethylbenzene and toluene at the active centers of the catalyst. The adsorption factor cannot, however, have any significance if the reaction has attained thermodynamic equilibrium; at this point toluene would act as an inert diluent, which shifts the position of the equilibrium point. Equal dilutions of ethylbenzene with nitrogen or toluene should in that case give equal yields of styrene.

The results of dehydrogenation of 4 ethylbenzene-toluene mixtures, containing 30, 50, 70, and 85 mol.-% of toluene, are given in Table 4. Molar velocity was calculated from the volume velocity and the density of the mixtures, on the assumption that density follows the addition rule. The depth of dehydrogenation was calculated from the expression 100a/b, where $\underline{a}$ is the styrene content of the catalyzate, and $\underline{b}$ is the ethylbenzene content of the original mixture. The results are shown in Column 11 of Table 4, and by the upper curve of Fig. 2.

TABLE 4

Dehydrogenation of Ethylbenzene Mixed with Toluene

No.	Composition of initial mixture				Volume velocity of mixture	Molar velocity of mixture	Degree of dilution n_{in}	Yield of catalyzate, as % of mixture introduced	Styrene content of catalyzate, as % by weight	% dehydrogenation of ethylbenzene		Difference
	% by weight		mol.-%									
	Ethylbenzene	Toluene	Ethylbenzene	Toluene						Found	Calc. from equa. (4)	
1	2	3	4	5	6	7	8	9	10	11	12	13
8	73.0	27.0	70.0	30.0	1.14	9.8	0.43	94	20.0	27.4	28.6	− 1.2
9	73.0	27.0	70.0	30.0	2.02	17.3	0.43	95	20.3	27.8	28.6	− 0.8
10	53.3	46.7	50.0	50.0	1.67	14.6	1.0	94	16.7	31.4	32.4	− 1.0
11	53.3	46.7	50.0	50.0	2.09	18.3	1.0	96	16.3	30.6	32.4	− 1.8
13	33.0	67.0	30.0	70.0	1.84	16.8	2.3	96	11.0	35.2	38.7	− 3.5
15	33.0	67.0	30.0	70.0	2.40	21.7	2.3	96	11.4	34.6	38.7	− 4.1
36	17.0	83.0	15.1	84.9	1.62	15.0	5.6	97	6.3	37.0	49.1	−12.1
37	17.0	83.0	15.1	84.9	2.16	20.0	5.6	97	6.3	37.0	49.1	−12.1

The differences between calculated (from equation 4) and experimental values for depth of dehydrogenation for mixtures containing 30.50, and 70 mol.-% of toluene are 0.8-1.2, 1.0-1.8, and 3.5-4.1%, respectively. It has already been pointed out that the corresponding differences with nitrogen as diluent do not exceed 1.3%. Dilution with toluene (up to 70 mol.-%) thus gives the same effect as with nitrogen. Toluene, in the same way as nitrogen, shifts the equilibrium point to the right, and adsorption of toluene at active centers of the catalyst does not significantly affect the depth of dehydrogenation of ethylbenzene.

When, however, the toluene concentration is raised to 85%, the difference between calculated and experimental values increases to 12%. This abrupt rise is ascribed to rapid inactivation of the active centers at high toluene concentrations. There are references in the literature [6] to rapid inactivation of the catalyst by toluene, and in particular by benzene (or, more probably, by the products of their transformation at the catalyst surface), and these observations agree with ours. We found that when equal portions of ethylbenzene-toluene mixture (70% toluene) are passed over the catalyst, the depth of dehydrogenation of ethylbenzene rises with increasing molar velocity (Table 5).

TABLE 5

Dehydrogenation of 3:7 ethylbenzene-toluene mixtures

Expt. No.	Ml of mixture passed before the experiment	Ml of mixture passed during the experiment	Volume velocity of the mixture	Molar velocity of the mixture	Yield of catalyzate as % of mixture introduced	Styrene content of catalyzate, as % of wt.	Depth of dehydrogenation, % found	Depth of dehydrogenation, % calcd. from equation (4)	Difference, %
1	2	3	4	5	6	7	8	9	10
14	8	10	1.00	9.0	93	10.1	30.6	38.7	−8.1
12	8	10	1.55	14.0	95	10.9	33.0	38.7	−5.7
13	11	12	1.84	16.8	96	11.6	35.2	38.7	−3.5
15	14	10	2.40	21.7	96	11.4	34.6	38.7	−4.1

It is of interest that the depth of dehydrogenation of undiluted ethylbenzene remains constant over the same range of molar velocities (Fig. 3). This difference may be explained as being due to rapid inactivation of the catalyst by the products of transformation of toluene; the faster the mixture passes over the catalyst, the less time is there for toluene or its transformation products to undergo adsorption at the active centers. Toluene thus influences the reaction in two ways: as an inert diluent it displaces equilibrium in the direction of styrene production, but by lowering the activity of the catalyst it reduces the velocity of the reaction. Hence the depth of dehydrogenation of ethylbenzene rises with increasing toluene content of the mixtures, but at the same time the difference between calculated and experimental values also rises.

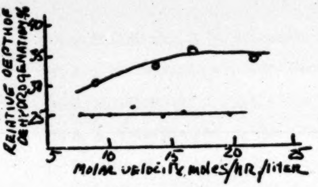


Fig. 3. Dehydrogenation of ethylbenzene without diluent, and diluted with toluene: ● - ethylbenzene without diluent; o - ethylbenzene - toluene mixture.

Discussion of Results

The results of this research may be summarized as follows. The yields of styrene obtained by dehydrogenation of ethylbenzene without a diluent are constant over a wide range of molar velocities. Dilution with hydrogen causes a sharp fall in the depth of dehydrogenation, the experimental values for which are only 3-4% higher than the calculated ones. The depth of dehydrogenation rises with increasing nitrogen content of the mixtures, and these values agree well with those derived from thermodynamic calculations; at equal dilutions the effects obtained with nitrogen or with toluene (up to 70%) are practically identical, showing that the reaction attains thermodynamic equilibrium, and hence that the effect of inert diluents is to shift the equilibrium point in the direction of styrene production.

However, not all the diluents usually considered as inert (CO_2, H_2O) are in fact inert. Thus it is known that the effluent gases obtained during dehydrogenation of ethylbenzene diluted with CO_2 contain up to 50% of carbon monoxide [3], which may arise by one of the reactions:

$$CO_2 + C = 2CO \text{ and } CO_2 + H_2 = CO + H_2O.$$

Both reqctions raise the dilution of the equilibrium mixture, owing to access of CO or H_2O, and thereby raise the yields of styrene. Apart from this, the oxidation of some of the hydrogen, and thus its removal from the reaction leads to a further displacement of the equilibrium. Tolstopyatova [4] found a greater depth of dehydrogenation of ethylbenzene with carbon dioxide at 575° than we did with nitrogen.

The opposite effect is obtained as a result of the reaction of steam with "coke": $H_2O + C = CO + H_2$; the hydrogen produced causes a fall in the yield of styrene. Our experiments showed that the yields of styrene were

2-2.5 times smaller when carbon dioxide in the mixtures was replaced by equal volumes of steam. Thus it appears that the yields of styrene obtained under the same conditions may vary according to the nature of the diluent, and the differences may be due to kinetic as well as to thermodynamic factors.

The results obtained afford further evidence that changes in the depth of reaction following dilution with inert substances or reaction products may be due not to differences in the adsorption constants but to the reaction attaining its equilibrium point. These results may serve for the critical revision of certain currently held views [1,3,4,5,6] on the role of inert diluents in the dehydrogenation of ethylbenzene.

SUMMARY

1. A study has been made of the reaction of catalytic dehydrogenation of undiluted ethylbenzene at 575°, and of its mixtures with hydrogen, nitrogen and toluene.

2. It is shown that the reaction attains a state of thermodynamic equilibrium over a wide range of flow velocities, and that the role of inert diluents depends on displacement of the equilibrium point.

Received November 16, 1951

Institute of Organic Chemistry
Academy of Sciences USSR

LITERATURE CITED

[1] B. N. Dolgov. Catalysis in organic chemistry. Goskhimizdat,* Moscow-Leningrad, 1949, p. 196.

[2] N. V. Shorygina. Styrene, its polymers and copolymers. Goskhimizdat,* Moscow-Leningrad, 1950, p. 12.

[3] N. D. Zelinsky, G. M. Marukyan, and O. K. Bogdanova. J. Appl. Chem. 14, 161 (1941).

[4] A. A. Tolstopyatova. J. Gen. Chem. 17, 2182 (1947).

[5] G. M. Marukyan. J. Appl. Chem. 19, 1277 (1946).

[6] A. A. Tolstopyatova. J. Gen. Chem. 18, 865 (1948).

[7] E. Mitchell, Trans. Am. Inst. Chem. Eng. 42, 293 (1946).

[8] G. M Marukyan. J. Appl. Chem. 19, 623 (1946).

[9] K. Rosenmund and W. Kuhnhenn, Z. Untersuch. d. Nahrungs-und Genussmittel 46, 154 (1923).

[10] G. M. Marukyan and A. A. Tolstopyatova. J. Appl. Chem. 19, 1079 (1946).

[11] M. Kh. Karapetyants. Chemical thermodynamics. Goskhimizdat,* Moscow-Leningrad, 1949, p. 370.

[12] O. Hougen and K. Watson. Physicochemical calculations in engineering. Goskhimizdat,* Moscow-Leningrad, 1941, p. 562.

[13] Technical encyclopedia. Handbook of physical, chemical, and technical values, vol. 7. Published by Soviet Encyclopedia, Moscow, 1931, p. 448.

---

* State Chemical Press

POISONING OF PLATINUM CATALYSTS WITH A LOW CONTENT OF ACTIVE METAL ON A CARRIER, UNDER CONDITIONS OF DEHYDROGENATION CATALYSIS

Kh. M. Minachev, N. I. Shuikin, and I. D. Rozhdestvenskaya

It has been firmly established that only very small amounts of poisons are required for the inactivation of catalysts, as is shown by a survey of the extensive literature of the subject [1,2,3].

According to N. D. Zelinsky [4] the cause of inactivation of metal-containing catalysts under conditions of hydrogenation or dehydrogenation catalysis, and in the absence of specific poisons, is the formation of the so-called "carbonaceous film" on the catalyst surface. This film arises by the partial decomposition of the substrates, and by occluding the active surface inhibits the catalytic reaction. Zelinsky showed that surfaces thus inactivated may be reactivated by the action of atmospheric oxygen [5].

Shuikin, Novikov, and Tulupova [6] found that rapid inactivation of a platinized charcoal dehydrogenation catalyst (5% Pt) took place with cyclopentadiene, 1-ethycyclopent-1-ene, and allylcyclopentane, but not with cyclohexene or alkenes. This effect was ascribed by the authors to partial dehydrogenation of five-membered cycles, to give labile dienes, the polymers of which occlude the active centers of the catalysts. In one of our earlier papers [7] we explained the fall in activity of platinum catalysts under conditions of occlusion of active centers by carboids as being due to the possibility of formation of qualitatively different active centers, able to promote fission of six-membered hydrocarbon rings, when large deformations of the crystal lattice exist. Freidlin and Ziminova [8] ascribe inactivation of catalysts to depromotion during the reaction.

Rubinshtein and Pribytkova [9], in studying the action of thiophen on Ni-Mg catalyst of dehydrogenation of cyclohexane or of hydrogenation of benzene, found that the more highly disperse catalysts are the more resistant to poisons. On the basis of changes in the energy of activation of the reaction of dehydrogenation of cyclohexane according to the amount of poison introduced, the authors draw certain conclusions regarding the mechanism of poisoning of catalysts (in the given case by chemosorption of the poison), and as to the heterogeneity of the catalyst surface.

We know from the work of Zelinsky et al. [10] that platinum catalysts used for aromatization of gasoline hydrocarbons are sensitive to the action of sulfur compounds contained therein. Thus Zelinsky and Shakhnazarova [11], in their study of poisoning of platinized charcoal by sulfur-containing compounds in cyclohexane at 300-350°, show that the dehydrogenating activity of the catalyst falls regularly, but its desulfurizing activity is retained. The catalyst is reactivated by passing pure cyclohexane; the hydrogen liberated combines with bound sulfur, removing it as hydrogen sulfide. Zelinsky [10] represents the processes of poisoning of catalyst by sulfur compounds, and of its regeneration, as follows:

$$R_2S + Me + H_2 \longrightarrow MeS + 2RH \qquad (1)$$

$$MeS + H_2 \longrightarrow Me + H_2S. \qquad (2)$$

Inactivation of the catalysts is, however, studied in the researches quoted above only qualitatively.

In planning this research on poisoning of platinum catalysts, consisting of small amounts of platinum on a carrier, we hoped to elucidate the following points:

(1) to determine the stability of catalysts of dehydrogenation of cyclohexane, according to the amount of poison introduced, and to the platinum content of the catalyst;

(2) to find the relationship between molecular structure of the poison and its inactivating power;

(3) to find changes in the energy of activation of the reaction of dehydrogenation of cyclohexane and in the pre-exponential term of the Arrhenius equation before and after poisoning of the catalysts

(4) to find whether the poisons cause any structural change in the catalysts; and

(5) to investigate the possibility of regenerating poisoned catalysts.

EXPERIMENTAL

Catalysts. The catalysts were prepared from activated charcoal, and contained 3.21, 1.41, 0.62 and 0.37% of platinum; only the concentration of chloroplatinous acid was varied, all other conditions being maintained uniform.

Poisons. The following catalyst poisons were used: n-propylmercaptan, isoamylmercaptan, thiophen, thiophan, diethyl sulfide, diisoamyl sulfide, hydrogen sulfide, and carbon disulfide.

Cyclohexane. This had b.p. 80.6°/760 mm, d_4^{20} 0.7779 and n_D^{20} 1.4263.

Apparatus. All experiments were performed under strictly standardized conditions. The reaction tube, diameter 14 mm, was placed in an electric oven 90 cm in length. 2.5 g of catalyst was placed in a layer 5.5-6 cm long, in the middle of the tube. The temperature was measured by means of a thermocouple placed at the center of the layer of catalyst; the temperature did not usually vary more than ±1° during the experiments. Cyclohexane was delivered to the reaction zone at a uniform rate, by means of an automatic burette with a piston propelled at a uniform rate by a synchronous motor. The gas was measured by a burete volume 1000 ml, graduated in 2 ml, with a constant level.

Experiments. The catalysts were reduced in a stream of electrolytic hydrogen at a temperature gradually rising to 310°, the process taking 4 hrs. Dehydrogenation of cyclohexane, with or without poisons, was conducted without addition of hydrogen. The effect of poisons was studied by passing 10 ml of cyclohexane containing 0.0005 g of organic sulfur, at 280°. The extent of conversion of cyclohexane into benzene was derived from refractive index measurements of the catalyzate and from measurement of the volume of hydrogen produced. After poisoning the catalysts (before determining their activity) the value of the activation energy of the reaction of dehydrogenation of pure cyclohexane (not containing poison) was determined, using poisoned catalyst. Activation energy was also determined for all catalysts before exposure to the poisons.

In the kinetic experiments, the levels of the piston and of the water in the gas pipet were read after the required temperature had been reached, and the experiment was begun. The gas was passed through for 10-15 min., during which time the temperature of the oven became constant. Measurements of the temperature, of the volume of gas produced, and of the amount of cyclohexane used were made every 5 min. The volume of hydrogen produced was reduced to NTP, taking into account the level of the water in the gasometer for each experiment. The length of the experiments varied from 45 to 100 min.

Kinetics of dehydrogenation of cyclohexane, using platiunum catalysts with different contents of metal, before their poisoning.

In order to elucidate the mechanism of poisoning of the catalysts it was necessary to compare the kinetics of the reaction with catalysts before and after poisoning. It had been established in preliminary experiments that the activity of the catalysts remains constant for a long time when used with pure cyclohexane. The gas evolved consisted of hydrogen with 1.5% of saturated hydrocarbons, apparently cyclohexane carried over by the strong stream of hydrogen. These results showed that we could take the volume of hydrogen produced in unit time as a measure of the velocity of dehydrogenation of cyclohexane. The rate of delivery of cyclohexane was in all cases 0.5 ml in 5 min. (volume velocity 0.65 liters per liter of catalyst per hr).

The results obtained are given in Table 1, and Fig. 1 represents the temperature dependence of velocity of reaction. The points obtained all lie on straight lines, showing that the reaction follows the Arrhenius equation. As appears from Table 1, catalysts containing 3.21 and 1.41% of Pt gave results (Q and K_0) differing by amounts close to the experimental error of the determinations. As the Pt content of the catalysts diminishes, the number of active centers rises relatively, being several times as great, for example, for catalyst No. 2 (1.41% Pt). These active centers are evidently of lower activity, since increase in the number of active centers is associated with an increase in activation energy of up to 3300 cal/mol, this result being considerably beyond the limits of experimental error.

Poisoning of catalysts

The time when hydrogen sulfide began to appear in the issuing gases was found by means of preliminary experiments. Qualitative reactions for thiophen in the catalyzate were negative, showing that the whole of the sulfur introduced was held on the catalysts. The tables and curves are based only on data obtained before appearance of hydrogen in the effluent gases, i.e., while the whole of the sulfur was still bound on the catalyst.

TABLE 1

Kinetic data for dehydrogenation of cyclohexane in presence of platinized charcoal catalysts containing different amounts of platinum

Platinum content of catalyst,%	Expt. No.	T	v_0 for 10 min.	x conversion,%	Q	K_0
1	2	3	4	5	6	7
3.21	29	473	80.6	13.8	14780	$3.38 \cdot 10^8$
	30	489	136.0	21.8		
	31	527	535.0	85.8		
	32	519	364.0	58.4		
1.41	77	515	348.8	56.0	15250	$1.66 \cdot 10^8$
	76	488	135.0	21.6		
	79	473	74.0	11.8		
	80	503	239.0	38.0		
	81	526	468.0	75.2		
0.62	59	536	432.0	69.4	17360	$8.52 \cdot 10^8$
	60	526	330.0	53.0		
	61	475	54.0	8.6		
	62	488	92.0	14.6		
	63	507	172.0	27.6		
	64	499	126.0	20.0		
	65	512	226.0	36.0		
	66	531	388.0	62.2		
0.37	98	539	481.2	77.2	18080	$1.07 \cdot 10^9$
	99	528	383.0	61.4		
	100	516	245.0	39.2		
	101	503	141.0	22.4		
	102	479	57.0	9.0		
	103	491	87.0	13.8		

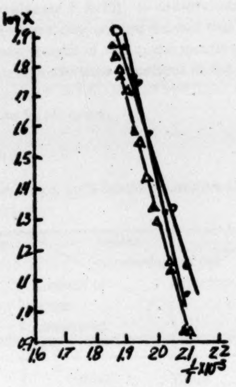


Fig. 1. Dependence of velocity of reaction on temperature, with the catalysts: o - 3.21% Pt on charcoal; ● - 1.41% Pt on charcoal; Δ - 0.62% Pt on charcoal; ▲ = 0.37% Pt on charcoal.

Tables 2 and 3 show % dehydrogenation of cyclohexane according to the amount of sulfur introduced, and to the nature of the sulfur-containing compound, and Fig. 2 gives typical poisoning curves. The introduction of 1-3 portions of poison has practically no effect on the activity of catalyst No. 1 (3.21% Pt). Successive further portions each lower the activity by 6-10%, but the activity is still considerable even after 11 portions. The general process of poisoning of the catalysts is much the same for all the sulfur-containing compounds, except for catalyst No. 1, which is inactivated more rapidly by one group of poisons (propyl mercaptan, isoamyl mercaptan, thiophen) than by another (diethyl and diisoamyl sulfide, thiophan, hydrogen sulfide).

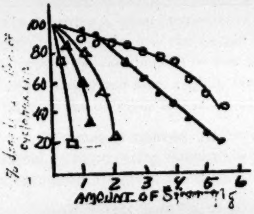


Fig. 2. Dependence of % dehydrogenation of cyclohexane on the amount of sulfur introduced: o - diisoamyl sulfide, catalyst No. 1 (3.21% Pt on charcoal); ● - n-propyl mercaptan, same catalyst; Δ - thiophen, catalyst No. 2 (1.41% Pt on charcoal); ▲ - n-propyl mercaptan, catalyst No. 3 (0.62% Pt on charcoal); □ - n-propyl mercaptan, catalyst No. 4 (0.37% Pt on charcoal).

It was of interest to compare these results with those obtained with catalysts poisoned with hydrogen sulfide. Catalysts No. 1 (3.21% Pt) and No. 2 (1.41% Pt) were poisoned with hydrogen sulfide, mixtures of which with hydrogen were passed together with cyclohexane through the catalysts. Passage of 3.8 ml of hydrogen sulfide (containing 0.0054 g of sulfur) through catalyst No. 1 reduced dehydrogenation of cyclohexane from 99.8%

(n_D^{20} of catalyzate 1.5000) to 27.8% (n_D^{20} of catalyzate 1.4418). Passage over catalyst No. 2 of 1.46 ml of hydrogen sulfide (0.0021 g of sulfur) reduces depth of dehydrogenation from 97.6% (n_D^{20} of catalyzate 1.4980) to 14.3% (n_D^{20} of catalyzate 1.4340). A comparison of the results obtained with hydrogen sulfide with those given by other sulfur-containing poisons showed that they all give approximately the same degree of inactivation of the catalysts per unit weight of sulfur, irrespective of the structure of the poison. It follows either that the mean life of the different molecules of poisons at the catalyst surfaces is the same, or that the catalysts decompose the various poisons with production of hydrogen sulfide at about the same rates, in which case the poison is actually hydrogen sulfide in all cases.

TABLE 2

Dependence of % dehydrogenation of cyclohexane on the amount of sulfur introduced into catalyst No. 1 (3.21% Pt)*

Expt. No.	Sulfur compound / Amount of sulfur introduced in g	% Dehydrogenation of cyclohexane						
		propyl mercaptan	isoamyl mercaptan	thiophen	diethyl sulfide	diisoamyl sulfide	thiophan	hydrogen sulfide
1	0.0005	98.6	98.0	97.6	96.0	95.0	93.8	98.6
2	0.0010	96.4	98.0	95.2	93.0	88.6	89.2	93.6
3	0.0015	96.8	96.0	96.6	89.2	86.2	88.6	92.3
4	0.0020	86.6	89.6	92.6	88.0	86.0	85.8	86.0
5	0.0025	72.4	74.3	87.0	87.7	83.0	82.4	82.4
6	0.0030	63.0	66.4	73.0	83.0	79.0	80.0	78.4
7	0.0035	53.6	63.0	62.4	76.6	76.6	77.0	73.0
8	0.0040	47.5	51.0	50.8	72.0	73.0	74.0	64.6
9	0.0045	37.8	42.3	39.4	64.6	62.0	58.8	53.0
10	0.0050	27.0	32.8	29.8	53.0	51.3	50.4	46.0
11	0.0055	19.4	25.8	20.0	36.0	40.3	40.8	30.0

---

* Volume of catalyst 10 ml, weight 2.5 g, containing 0.0830 g of platinum, volume velocity of reaction mixture 0.65.

Calculations based on our experimental data show that the amount of sulfur which had to be added in order to lower the activity by 70-80% amounted to 5-7% of the weight of active metal contained in the catalyst, corresponding with 3 atoms of platinum per atom of sulfur.

Dependence of poisoning of catalysts on nature of carrier.

The results described above show that the amount of sulfur required to poison platinum catalysts with charcoal carrier is quite considerable in relation to the content of highly dispersed platinum. It was hence thought that the nature of the carrier may play a significant role in the process of inactivation of the catalysts. This possibility was checked on two catalysts, in which the carrier was silica gel or ultra-porous glass. These catalysts were much more rapidly inactivated by sulfur compounds than were those with charcoal carriers. The stability of the catalysts fell in the series charcoal, silica gel, porous glass carrier.

Poisoning of catalyst No. 5 (1% Pt on silica gel) was studied under the same conditions as for platinized charcoal catalysts, using thiophen as the poison; 7.75 g of catalyst, containing 0.0775 g of platinum, were taken, and the results are given in Fig. 3.

As is evident from Fig. 3 only 0.0022 g of sulfur is required to inactivate this catalyst, as compared with 0.0055 g, or nearly 2.5 times as much for a charcoal catalyst of about the same platinum content.

Kinetic data for dehydrogenation of cyclohexane before and after poisoning of platinized silica gel catalyst are given in Table 4, and Fig. 4 gives the velocity-temperature curves. A comparison of the values of Q and K_0 before and after poisoning shows that the fall in activity of the catalyst is in this case also due exclusively to the reduction in the number of active centers (cf. kinetic data for dehydrogenation in presence of platinized charcoal); the energy of activation remains the same after poisoning, while K_0 falls noticeably.

TABLE 3

Dependence of % dehydrogenation of cyclohexane on the amount of sulfur introduced into the catalysts*

Catalyst	Sulfur Compound / Amount of sulfur introduced in g	% Dehydrogenation of cyclohexane						
		propyl mercaptan	isoamyl mercaptan	thiophen	diethyl sulfide	diisoamyl sulfide	thiophan	hydrogen sulfide
No.2 (1.41% Pt) containing 0.0353 g of platinum	0.0005	96.0	92.6	92.8	90.0	93.4	95.0	92.4
	0.0010	86.0	85.0	81.0	86.6	87.0	78.0	85.0
	0.0015	56.0	55.8	54.8	55.0	56.0	51.0	65.0
	0.0020	30.0	28.0	25.0	19.4	18.8	21.5	44.6
	0.0025	–	–	–	–	–	–	20.1
No.3 (0.62% Pt) containing 0.0155 g of platinum	0.00025	83.6	85.9	–	–	86.0	84.0	–
	0.00050	62.0	63.4	–	–	61.8	65.2	–
	0.00075	35.0	30.5	–	–	34.8	38.5	–
No.4 (0.37% Pt) containing 0.0093 g of platinum	0.00025	73.4	–	72.8	–	71.5	75.2	–
	0.00065	21.7	–	16.8	–	19.4	20.4	–

---

* Volume of catalyst 10 ml, weight 2.5 g, volume velocity of reaction mixture 0.65.

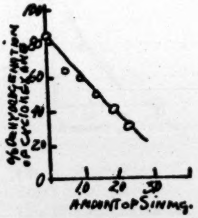


Fig. 3. Dependence of depth of dehydrogenation of cyclohexane on the amount of sulfur introduced. Catalyst No. 5 (1% Pt on silica gel):

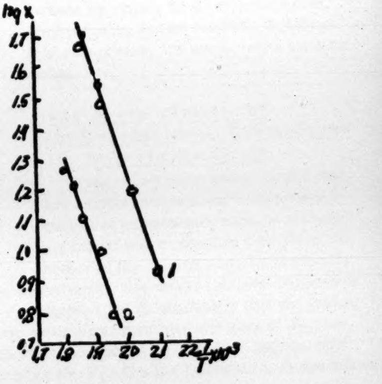


Fig. 4. Relation between velocity of dehydrogenation of cyclohexane and temperature, on catalyst No. 5 (1% Pt on silica gel): 1) before poisoning; 2) after poisoning.

Poisoning of catalyst No. 6 (1.08% Pt on porous glass). The catalyst was poisoned with thiophen under the same conditions as for the preceding catalysts, 13 g of catalyst containing 0.1404 g of platinum being placed in the reaction tube. The results are represented in Fig. 5, from which it appears that poisoning of this catalyst requires only 0.0020 g of sulfur, i.e. 2.75 times less than for catalyst No. 1, although catalyst No. 6 contains 1.75 times more platinum.

TABLE 4

Kinetic data for dehydrogenation of cyclohexane in presence of platinized silica gel.

Expt. No.	T	v_0 for 10 min.	x dehydrogenation, %	Q	K_0
		Before poisoning			
1	537	344.0	52.0	14600	$4.909 \cdot 10^7$
2	521	233.0	35.4		
3	494	103.8	16.0		
4	478	56.4	8.6		
5	521	200.1	31.0		
6	538	318.0	48.5		
		After poisoning			
16	555	121	18.6	14650	$1.253 \cdot 10^7$
17	538	83	13.0		
18	523	65	10.0		
19	510	40	6.0		
20	547	110	16.5		

The experiments show that the nature of the carrier profoundly affects the sensitivity of the catalysts to the action of poisons. The relatively high stability of platinized charcoal, as compared with platinized silica gel or glass, is connected with both the nature of the carrier and with its specific surface.

Poisoning of catalyst No. 2 (1.41% Pt) with carbon monoxide. The effect of carbon monoxide on platinized charcoal under conditions of dehydrogenation catalysis has not yet been studied. We conducted our experiments at 280 and 300°. The rate of delivery of cyclohexane and the amount of catalyst taken were the same as for the experiments on poisoning with sulfur-containing substances. In each experiment 10 ml of cyclohexane and 100 ml of carbon monoxide were passed over the catalyst. The results obtained are represented in Figure 6, from the curves of which it appears that at 280° the activity of the catalyst falls to less than half after passing 91.4 ml of carbon monoxide, and then falls by another 10-12%, after which it remains constant.

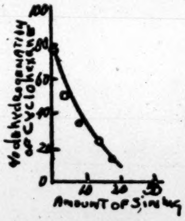


Fig. 5. Dependence of depth of dehydrogenation of cyclohexane on the amount of sulfur introduced. Catalyst No. 6 (1.08% Pt on glass).

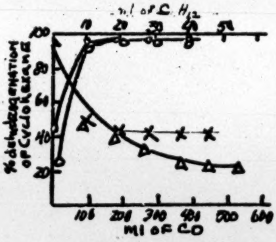


Fig. 6. Poisoning and regeneration of a catalyst containing 1.41% Pt on charcoal: × – poisoning with CO at 300°; Δ – poisoning with CO at 280°; ● – regeneration of catalyst poisoned at 300°; ○ – regeneration of catalyst poisoned at 280°.

A somewhat different picture is given by experiments at 300°; the first portions of poison lower activity to about the same extent as at 280°, but further portions of carbon monoxide caused no more lowering of activity. Catalyst poisoned with carbon monoxide very quickly regains its former activity; thus the activity of the catalyst is fully restored by passing 20 ml of cyclohexane, after poisoning at 280 and 300°. It follows that carbon monoxide exerts only a transient action.

Study of the Kinetics of Dehydrogenation of Cyclohexane With Poisoned Catalysts

Preliminary experiments showed that when cyclohexane is passed over poisoned catalysts at temperatures equal to or lower than that at which poisoning took place the activity of the catalyst remains practically unaltered. The results obtained are given in Figures 7 and 8, which show that the volume of hydrogen evolved increases linearly with time. These preliminary experiments permitted the study of the kinetics of dehydrogenation of cyclohexane with Catalyst No. 1 (3.21% Pt-C) after poisoning with three poisons, with Catalyst No. 2 (1.41% Pt-C) poisoned with two poisons, and with Catalyst No. 3 (0.62% Pt-C) poisoned with one poison.

The experimental results so obtained are given in Table 5 and in Figure 9, which shows dependence of velocity of reaction on temperature. The points are all on straight lines, showing that the reaction follows the Arrhenius equation. A comparison of the values of activation energy for the catalysts before poisoning (Table 1, column 6) and after poisoning (Table 5, column 6) shows that they remain practically unaltered. Thus changes in the activity of the catalysts must be due only to change in the number of active centers, as is shown by the constancy of the activation energy and by the change in the value of K_0 in Arrhenius' equation. Comparison of the values of K_0 for catalysts before poisoning (Table 1, column 7) and after poisoning (Table 5, column 7) shows that K_0 for poisoned catalysts is 4.3 to 22.4 times smaller than their initial values, while the activation energies remain practically constant.

It follows from the results presented that our catalysts are highly homogeneous with respect to their properties.

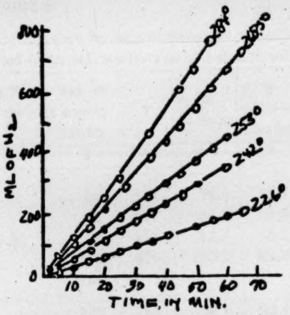


Fig. 7. Dependence of volume of hydrogen evolved on time; catalyst (3.21% Pt-C) after poisoning with thiophan.

X-Ray Data for the Catalysts Studied*

The structure of the catalysts used in this research was studied roentgenographically, before and after they had been poisoned with various sulfur-containing substances. The roentgenograms show that the phase composition of the catalysts is not changed by poisoning, and that they contain only one crystalline phase – platinum. The results are given in Table 6.

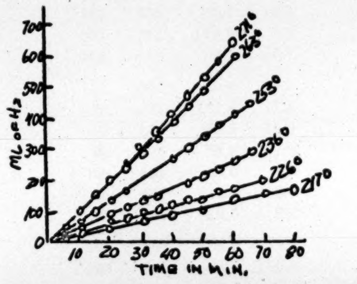


Fig. 8. Dependence of volume of hydrogen evolved on time; catalyst (1.41% Pt-C) after poisoning with n-propyl mercaptan.

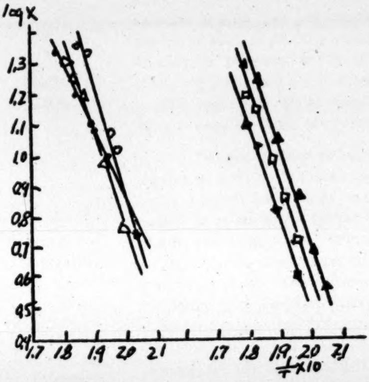


Fig. 9. Dependence of the velocity of dehydrogenation of cyclohexane on temperature, using catalysts poisoned with various substances: O – propyl mercaptan (catalyst No. 1; 3.21% Pt-C); ● – thiophen (same catalyst); △ – diethyl sulfide (same catalyst); ▲ – propyl mercaptan (catalyst No. 2; 1.41% Pt-C); – thiophen (same catalyst); ☐ – propyl mercaptan (catalyst No. 3; 0.65% Pt-C).

The platinum crystal lattice for catalysts containing less than 1% of platinum was an expanded one; this is characteristic of catalysts containing solid solutions of hydrogen, which would be formed in the special conditions of our experiments. A comparison of the lattice constants before and after poisoning shows clearly (in accordance with the absence of additional lines on the roentgenograms) that poisoning is not due to formation of compounds or solid solutions of the poison with platinum. The results of the X-ray studies agree well with the earlier described experiments establishing the constancy of Q and the variability of K_0 in the Arrhenius equation.

It follows that both structural and kinetic data indicate that the mechanism of poisoning is one of blocking of active centers, but not of chemosorption.

Regeneration of Poisoned Catalysts

The regeneration of poisoned catalysts is a very important problem in heterogeneous catalysis practice.

---

* We wish to express our gratitude to Doctor of Chemical Sciences A.M.Rubinshtein, who conducted the roentgenographic study of the catalysts.

TABLE 5

Kinetic data for dehydrogenation of cyclohexane in presence of platinized charcoal catalysts poisoned with sulfur-containing substances

% Pt in catalysts	No. of experiments	T	$\underline{v_0}$ for 10 min.	$\underline{x}$, % dehydrogenation	Q	K_0	Catalyst poison
1	2	3	4	5	6	7	8
3.21	50	513	72.0	11.7	16046	$7.81 \cdot 10^7$	Propyl mercaptan
	51	507	64.6	10.5			
	52	491	33.4	5.5			
	53	529	135.0	22.0			
	54						
3.21	262	554	136.6	22.0	15220	$4.57 \cdot 10^7$	Thiophan
	263	541	112.0	18.0			
	264	526	76.0	12.0			
	265	515	60.0	9.9			
	266	526	81.0	13.0			
3.21	384	553	125.0	20.6	15080	$2.29 \cdot 10^7$	Diethyl sulfide
	383	543	113.0	18.0			
	384	535	97.8	16.0			
	356	530	89.0	15.0			
	387	515	59.0	9.5			
	388	500	30.0	6.0			
1.41	91	557	120.4	19.5	15360	$2.51 \cdot 10^7$	Propyl mercaptan
	92	545	107.6	17.6			
	93	536	98.2	16.0			
	94	526	68.8	11.3			
	95	509	44.6	7.3			
	96	490	22.4	3.6			
	97	499	29.6	5.0			
1.41	282	557	96.0	15.7	16000	$3.74 \cdot 10^7$	Thiophan
	283	547	94.0	15.0			
	284	531	59.0	9.6			
	285	520	42.2	7.0			
	286	510	32.4	5.3			
0.62	70	555	77.4	12.7	16360	$3.82 \cdot 10^7$	Propyl mercaptan
	71	529.3	40.2	6.6			
	72	512	24.8	4.0			
	73	545	67.0	10.9			

TABLE 6

Changes in the crystal lattice constants of platinum in different samples of catalysts before and after poisoning

% Pt in catalysts	α_{Pt} before poisoning, in A	α_{Pt} after poisoning in A
0.37	4.09	4.020
0.62	3.998	3.914
1.41	3.910	3.890
3.21	3.880	3.850

Experiments were done on regeneration by means of cyclohexane of three platinum catalysts on different carriers poisoned with thiophen. Cyclohexane was passed at a volume velocity of 0.65 l per l of catalyst per hr. at 300°, in 10 ml portions. The results, presented in Fig. 10, show that platinized charcoal very quickly regains its initial activity, after passage of 70 ml of cyclohexane.

Platinized silica gel also regains its activity, although the initial value is not restored; activity cannot be raised to the initial value of 84% dehydrogenation. Practically no regeneration of platinum on porous glass takes place. This difference in the behavior of platinum catalysts on different carriers after poisoning with the same substance is of considerable interest; the reason for the differences is not clear, and further studies are required.

SUMMARY

1. Poisoning by means of sulfur-containing compounds of dehydrogenating catalysts consisting of different concentrations of platinum on various carriers has been studied. The effect of all the poisons is equal to that of an equivalent amount of hydrogen sulfide.

2. The structure of the poison molecule does not affect its action, suggesting that they are all decomposed at the catalyst surface at about the same rate, with production of hydrogen sulfide.

3. The amount of organically combined sulfur required to poison the catalysts is proportional to the amount of platinum contained therein.

4. The amount of sulfur required to lower the activity of catalysts by 70-80% is about 6-7% of the weight of platinum present on the carrier.

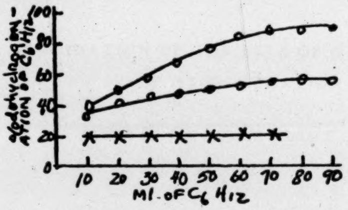


Fig. 10. Regeneration by means of cyclohexane of catalysts poisoned with thiophen: o - catalyst 1.41% Pt-C; middle curve - catalyst 1.0% Pt on silica gel; x - catalyst 1.08% Pt on glass.

5. The regenerability of platinum catalysts poisoned with one and the same substance varies according to the nature of the carrier.

6. It has been shown experimentally that the activation energy of the reaction of dehydrogenation of cyclohexane is the same for poisoned and unpoisoned catalysts. The value of the pre-exponential term of the Arrhenius equation is ten times smaller for poisoned than for fresh catalysts. These data, together with crystal lattice data, indicate that poisoning of platinum catalysts is due to occlusion of active centers.

Received March 10, 1952

Institute of Organic
Chemistry
Academy of Sciences
USSR

LITERATURE CITED

[1] M. Baccaredda, Handbuch der Katalyse, Bd. VI, Heterogene Katalyse. III. Vergiftung der Kontakte, Wien, 1943, p. 235-296.

[2] S. Berkman, D. Morrell, and G. Egloff. Catalysis in inorganic and organic chemistry. Vol. 1, p. 382. Moscow-Leningrad, 1949.

[3] V. P. Kamzolkin and V. D. Livshits. J. Applied Chem. 14, 1225 (1937); I. E. Adadurov and M. A. Gushinskaya, J. Appl. Chem. 5, 722 (1932).

[4] N. D. Zelinsky. Tech.-Economic J., 5, 854 (1925); Selected works, Vol. 2, p. 7. Moscow-Leningrad, 1941.

[5] N. D. Zelinsky and M. B. Turova-Polyak. Ber., 59, 156 (1926).

[6] N. I. Shuikin, S. S. Novikov, and E. D. Tulupova. Bull. Acad. Sci. USSR, Div. Chem. Sci. No.1, 89 (1947).

[7] A. M. Rubinshtein, Kh. M. Minachev, and N. I. Shuikin, Proc. Acad. Sci. U.S.S.R. 67, 287 (1949).

[8] L. Kh. Freidlin and N. I. Ziminova. Proc. Acad. Sci. 76 , 551 (1951); Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 6, 659 (1950); Proc. Acad. Sci. U.S.S.R., 74, 955 (1950).

[9] A. M. Rubinshtein and N. A. Pribytkova. Proc. Acad. Sci., U.S.S.R., 61, 285 (1948); A.M. Rubinshtein. Problems of kinetics and catalysis, No.6, p. 127. Acad. Sci. U.S.S.R. Press, Moscow, 1949.

[10] N. D. Zelinsky, I. A. Musaev, and G. D. Galpern. Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 2, 467 (1937); N. D. Zelinsky. Selected works, Vol. 1, p. 600. Moscow-Leningrad.

[11] N. D. Zelinsky and E. M. Shakhnazarova. Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 3-4, 571 (1936).

BLANK
PAGE

ELUCIDATION OF THE ROLE OF VARIOUS ADSORPTIONAL CENTERS IN THE REACTION OF HYDROGENATION OF ACETYLENE ON METALLIC NICKEL

STUDY OF THE ACTIVE SURFACE OF NICKEL BY MEANS OF A DIFFERENTIAL ISOTOPE METHOD

N. P. Keier

The differential isotope method of Keier and Roginsky [1-4] gives unambiguous evidence of the reality of the existence of inhomogeneities of active centers of adsorption, from activation energies and heats of adsorption for a number of typical catalysts and adsorbents. This allowed us to make a definite choice between "repulsion and inhomogeneity" when considering kinetic and equilibrium isotherms different from those found for uniform surfaces.

The experimental proof of the existence of inhomogeneity of active surfaces was of fundamental importance for the theory of adsorption and catalysis. For contact catalysts with proven heterogeneous surfaces, however, there still remained to be solved an even more difficult, but not less fundamental, problem, viz., to determine to what extent adsorptional centers with different heats of adsorption and with different activation energies actually take part in the catalytic process. In spite of the basic importance of the solution of this problem for the clarification of the intimate mechanism of catalysis, and for the elaboration of a theory of the velocity of catalytic processes, it has remained unsolved, owing to the lack of a direct method for its study. The differential isotope method, in combination with a study of the statistics of the active centers and of the kinetics of the reactions, now affords us all the necessary means for the solution of the problem.

The present paper presents the results of a study of the role of different active centers for adsorption of acetylene on metallic nickel, in the reactions of catalytic hydrogenation and methane formation.

EXPERIMENTAL

The method depended on the study of processes taking place in the adsorption layer when two successive portions of gas were passed, of which one contained a labelled stable or unstable isotope. If the reaction is of the type $2ABC \longrightarrow AB + C + A + BC$, adsorption is followed by desorption with small portions of gas. The isotope content of each component of the desorbed gas is then determined, and from this can be deduced from which adsorbed part of the gas the given component was formed. These experiments give a qualitative indication of the active centers at which the reaction takes place, and in which direction it goes. In the study of reactions of the type $A + B \longrightarrow AB$ adsorption of one of the components takes place in two portions, of which one contains labelled atoms. The catalyst is then treated with small portions of the second component, as a result of reaction with which the reaction products are evolved in the gaseous phase. Their isotope content is then determined, and from this it is concluded with which portion of adsorbed gas the second component had reacted. Knowing the dependence of the change in activation energy of adsorption on degree of filling of active centers it is possible to deduce at which centers of adsorption the catalytic reaction had taken place. The change in activation energy according to degree of saturation is derived from adsorption measurements.

1. Experimental methods

The nickel used was prepared by the method of Bag and Egupov, depending on extraction with alkali of a 1:1 nickel-aluminum alloy.* The given catalyst had a surface of 15± 1 sq.m. per g, as estimated from the adsorption isotherm for benzene. Before each experiment, the weighed portion of catalyst was degassed at 300° and reduced with hydrogen at the same temperature (the catalyst surface underwent partial oxidation even when it was stored under water), and was finally exhaustively degassed at $500°/10^{-5}$ mm.

Ordinary acetylene was prepared from chemically pure calcium carbide, and was purified by repeated fractionation in a vacuum apparatus. Acetylene labelled with C^{14} was prepared from labelled barium carbide, obtained from labelled barium carbonate by heating with magnesium by Maquenne's method [5]. We determined a temperature regime for this reaction, which ensured a 75-85% yield of acetylene, calculated on the carbon taken. Ordinary ethylene was prepared by dehydration of ethanol over a catalyst. Hydrogen and oxygen were prepared electrolytically, and were freed of traces of oxygen or hydrogen, respectively, by their combustion on palladized silica gel.

---

* The author takes the opportunity of thanking G. V. Isagulyants for providing him with the catalyst.

The C^{14} content was derived from measurement of the radiation of barium carbonate, by means of a counter with a mica window, thickness 4 mg/sq.cm. The specimens under measurement were placed on filter paper discs 2 cm in diameter, and the radiation was compared with that of standard specimens obtained under identical conditions from the original labelled acetylene. It was necessary, owing to the softness of the C^{14} radiation, to introduce a correction for its absorption by the emitting sample itself; this was effected by means of a calibration curve connecting specific activity of specimens of barium carbonate prepared from labelled acetylene with weight of precipitate. The C^{14} content of any carbonaceous gas was determined by burning it at an electrically heated platinum wire, and absorbing the carbon dioxide so produced in aqueous barium hydroxide, which was then filtered, to collect barium carbonate.

The apparatus used is shown in Fig. 1. The part B beyond the cocks 14 and 13 served for burning the gas under analysis and for absorbing the resulting carbon dioxide. Before introducing the gas, this part of the apparatus, with the absorption tube 6 attached, as shown in Fig. 1, was exhausted to a vacuum of 10^{-5} mm, and the gas was transferred from the reaction vessel 1 into the combustion vessel with the aid of a special diffusional mercury-condensational pump 5. The oxygen needed for combustion was taken from flask 7, at a pressure controlled by the manometer 8, in amount in excess of that required. The carbon dioxide formed was frozen out of the combustion gases, in a side-tube of the combustion vessel, and was then transferred to the trap 9, from which it was removed by means of a stream of CO_2-free nitrogen, which swept it into the absorbent tube 6, the construction of which is clear from Fig. 1.

The cocks 10 and 11 were closed when all the carbon dioxide had been swept out, and the baryta water was slowly passed through the filter, to collect barium carbonate. The filter paper with precipitate was dried to constant weight before measurement of its β-radiation. The overall error in determining specific β-activity was taken as being identical with the error involved in determining the weight of the precipitate *, since the error incurred in measuring β-activity by means of a counter may be made vanishingly small, by prolonging the time of counting. The accuracy thus varied according to the amount of precipitate formed, the error amounting to ±20% or more for precipitates weighing 0.5 mg or less, ±10% for 1 mg, and ±2% for 5 mg.

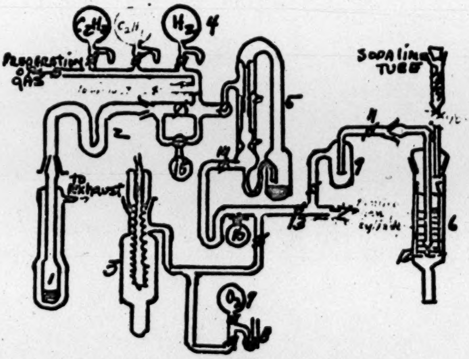


Fig. 1. Sketch of apparatus: 1) reaction vessel; 2) trap; 3) vessel for combustion of gases under analysis; 4) flasks for storage of gases; 5) mercury diffusional pump; 6) absorber; 7) flask; 8) manometer; 9) trap; 10-14) cocks; 15-16) McLeod manometers.

Analysis of gas. The acetylene content of its mixtures with ethylene and ethane was determined by its adsorption on nickelous oxide, prepared by the thermal decomposition of thoroughly washed nickel carbonate. Adsorption proceeded with great rapidity, at a velocity many times greater than that of ethylene, which could be totally eliminated by heating the oxide in vacuum at 400° for 3-4 hrs. The partial pressure of acetylene did not exceed 10^{-4} mm after the separation. Ethylene was quantitatively separated from ethane by absorption in a solution of $HgSO_4$ in sulfuric acid.

---

* The inaccuracy in the determination of the weight of the precipitates is connected with their variable water content, resulting from their hygroscopicity, and amounting to 0.5-0.1 mg.

2. Study of active surface by means of the differential isotope method

In distinction to ethylene, which was not adsorbed in appreciable amount by our catalyst, acetylene was actively adsorbed, in appreciable amount, at room temperature and below. Adsorption of acetylene was studied in static conditions in a vacuum apparatus, applying a previously described procedure [6-7], without any modification. Our first experiments showed us that only a part of the acetylene is adsorbed reversibly; the amount irreversibly adsorbed varies according to the activity of the given catalyst. Up to 40% of the surface of a specimen of nickel placed in the reactor in a damp condition bound acetylene irreversibly, as compared with only about 10% when the catalyst was first dried in a current of nitrogen; total adsorption in the latter case was also much smaller. The surfaces of the two specimens were approximately equal, as determined from the equilibrium isotherms for adsorption of benzene.

Desorption at over 150°.of acetylene adsorbed at room temperature leads to evolution of methane and hydrogen, together with acetylene, although evolution of hydrogen was not observed during the adsorption process. At 500° it was found that 30% of adsorbed ethylene was recovered unchanged, and of the remaining 70% about 14% was accounted for by production of methane. The remaining acetylene underwent decomposition with production of hydrogen.

Experiments involving the application of the differential isotope method were applied to investigation of the uniformity of the active centers. Two portions of acetylene were adsorbed successively on a weighed amount of catalyst. The first portion consisted of ordinary acetylene, using 1.267 ml per g, and the second was labelled acetylene, (0.148 ml per g), being 90% and 10% of the total amount adsorbed, respectively. After completion of adsorption the reaction vessel was exhausted to a vacuum of 10^{-4} mm, for 2 min., after which desorption was effected by raising the temperature, simultaneously evacuating the desorbed gas from the reaction vessel to the space B by means of pump 5 (Fig.1), which maintains a vacuum of 10^{-4}mm over the catalyst. In the portion of acetylene desorbed at up to 55°, representing less than 3% of the amount adsorbed, specific activity was only 3± 0.5% of that of the original labelled acetylene, adsorbed in the second portion. It may be concluded that the desorbed gas originates, to about 97%, from the first portion of gas adsorbed. The further portions of desorbate, containing methane and hydrogen, were not analyzed.

It follows from the results of this experiment that the surface is not uniform; if it had been, the probability of desorption of any molecule originating from the first or second portions of gas would have been equal, and the desorbed gases should have contained about 10% of labelled carbon compounds, whereas in fact they contained only 3%. It follows that there is no simple relationship between the activation energies of adsorption and desorption. This conclusion was confirmed by further experiments with labelled acetylene.

In these experiments, two, and in some cases three, portions of labelled and ordinary acetylene were passed over the prepared catalyst surface, in different orders. The first portion was usually totally adsorbed, while the second was adsorbed more slowly; the process was in many cases interrupted by pumping off the residual gas.

The first portion of hydrogenation products was removed from the surface at room temperature, by placing the catalyst with adsorbed acetylene in contrast with hydrogen. As a result, ethane and ethylene are formed, the former not being adsorbed on the catalyst, and the latter only very slightly. A considerable part of the hydrogen taken undergoes adsorption, without being used for hydrogenation.

The reaction gas thus obtained, under conditions of excess of hydrogen, consists chiefly (85-90%) of ethane. It was noticed that the ethylene content of the first portion of desorbed gas was lower than in subsequent ones. The whole of the adsorbed acetylene which is capable of hydrogenation does so at room temperature. Ethane and ethylene were usually absent from the gas obtained by treatment with hydrogen at higher temperatures, up to 200°; it contained methane, together with some acetylene which did not under these conditions undergo hydrogenation. In order to be sure that hydrogenation takes place at those active centers at which adsorption had taken place, but that it does not take place at some other kind of active center, to which the acetylene found in the desorption gas had been bound, a number of experiments were performed, in which prolonged desorption was carried out at room temperature, before admission of hydrogen, freezing out the acetylene in a special trap.

All the gaseous products obtained by the above methods from the catalysts were analyzed for their C^{14} content; ethane and ethylene were analyzed together. Knowing the C^{14} content it is possible to estimate how much each succeeding portion of acetylene had contributed towards the formation of the given reaction product. Analysis showed that with low degrees of saturation of the surface, up to 30%, there is no exchange of acetylene molecules adsorbed from the first portion of gas with those of the unadsorbed part of the second portion, although this does take place to a small extent (up to 5%) with higher saturations. The experimental results are presented

in Table 1; the catalyst was metallic nickel introduced wet into the reaction vessel. *

The first experiments showed that not all centers of adsorption are catalytically active for the hydrogenation reaction. If the probability of reaction of all adsorbed molecules were the same, we should expect the C^{14} content of any of the portions of ethane obtained to be equal to the mean value for adsorbed acetylene; we found that this was never the case. Thus in Experiment 12 two portions of acetylene were adsorbed on 0.65 g of catalyst. The first portion consisted of 2.81 ml of ordinary acetylene, sufficient to cover 48% of the catalyst surface (the area occupied by 1 molecule of acetylene was taken as $6 \cdot 10^{-16}$ sq. cm.), and the second was 1.23 ml of labelled acetylene, covering 20% of the surface; the average content of labelled acetylene in adsorption was 30%.

In this experiment, the pressure over the catalyst was lowered to 10^{-4} mm for 1 min. before admitting hydrogen. Ethane and acetylene in the issuing gases were separated out by freezing in liquid nitrogen. The ethane was separated, and transferred to the combustion vessel, and its C^{14} content was determined; it was found to be 57 ± 2% of its amount in the initial portion of labelled acetylene. Hence this portion of ethane contained 43% of hydrogenated acetylene molecules from the ordinary acetylene adsorbed from the first portion, and 57% from the second. Altogether, 4.6% of the adsorbed acetylene underwent hydrogenation in this portion.

A second portion of hydrogen left in contact with the catalyst for a long time at room temperature hydrogenated only 0.8% of the adsorbed acetylene, the gas evolved not being analyzed. A third portion was obtained by heating at up to 150° in presence of hydrogen, and in these conditions acetylene was desorbed; almost all of this (94 ± 1%) was derived from the second, labelled portion of acetylene. With further rise in temperature, in absence of hydrogen, a gas not containing constituents condensing at −182° was obtained, and this gas was shown to consist of methane and hydrogen. It contains mainly methane at 150-200°, but the hydrogen content rises with increasing temperature above this. The virtual absence of C^{14} (3 ± 0.3%) from methane desorbed at 400° testifies to its origin from the first portion of adsorbed acetylene.

This experiment thus suggests the presence of three groups of active centers: (1) active centers at which reversible adsorption of acetylene takes place, but not its hydrogenation, (2) active centers of adsorption at which hydrogenation takes place, and (3) active centers of adsorption at which formation of methane and hydrogen takes place.

It was thought to be of interest to find the energy of activation of adsorption at the centers where methane is formed. With this object, in experiment 13 three successive portions of acetylene were adsorbed, instead of the usual two; the first consisted of 0.328 ml of labelled acetylene (about 16% of the total amount adsorbed), the second of 1.142 ml (54.6% of total adsorbed) or ordinary acetylene, and the third of 0.619 ml (about 30% of total adsorbed) of labelled acetylene. In this experiment the first portion of gas was subjected to desorption for 170 min. at room temperature, during which time only 4% of the amount adsorbed had been removed; the corresponding figures for the second and third portions were 2.4% and 1.6%. Desorption was then continued for a further 15 hrs. at room temperature, but the amount of gas so collected was insufficient for analysis. The next portions of gas were removed by hydrogenation at room temperature; about 2.5% of the adsorbed acetylene underwent hydrogenation during 288 min. The ethane (containing traces of ethylene) so formed was derived (66%) from the second and (34%) third portions of acetylene.

As in the previous experiments, raising the temperature to above 100° leads to evolution of acetylene and methane, with a small amount of hydrogen. The acetylene had a higher C^{14} content, as compared with that of the ethane. Determination of the C^{14} content of the methane showed that it was formed chiefly from the carbon of the second portion of adsorbed acetylene. The higher the temperature, the lower is the C^{14} content of the methane. Thus the methane collected over the interval 100-200° contains 10 ± 1% of its carbon derived from labelled acetylene, while in the following three portions evolved at temperatures up to 500°, the C^{14} content falls to zero. Less than half of the carbon of adsorbed acetylene is found in the gases released at up to 500°, nor do they contain any carbon derived from the first portion of acetylene adsorbed.

This experiment shows clearly that methane is formed at active centers of intermediate, but not of minimum, activation energies, these energies being lower than for those associated with reversible adsorption of acetylene, at which hydrogenation also proceeds. It appears from experiments 14 and 12 that hydrogenation proceeds for the given specimen of nickel at adsorptional active centers corresponding with 42-48% saturation of the surface. At higher saturations acetylene is reversibly adsorbed, but does not enter into reaction, while at

---

* The catalyst, having pyrophoric properties, was usually stored under water.

TABLE 1

Expt. No.	Sample No.	% Content of labelled acetylene carbon	Gas	Temp.°C	Amount of carbon removed from adsorption %	Method of removal	Conditions of adsorption of acetylene
12	1	57± 2	Ethane + acetylene	Room	4.6	Hydrogenation	Weight of catalyst 0.65 g
	2	Not analyzed	Ditto	Ditto	0.76	"	I. 2.81 ml of ordinary acetylene adsorbed; saturation of surface 45.3%
	3	96± 1	Acetylene	120-150	–	Heating, + H_2	
	4	Not analyzed	Methane + H_2	200	–	Heating	II. 1.23 ml of labelled acetylene adsorbed; saturation of surface 19.8%
	5	"	Ditto	300	–	Ditto	
	6	3± 0.3	"	400	–	"	Average content of labelled acetylene at the surface 30%
13	1	40± 1	Acetylene	Room	4.0	Desorption	Weight of catalyst 0.65 g, from Experiment 12
	2	34± 3	Ethane + acetylene	Ditto	2.4	Hydrogenation	I. 0.328 ml of labelled acetylene adsorbed; 15.7% of total adsorbed acetylene.
	3	60±1	Acetylene	50-100	9-10	Desorption	
	4	10±1	Methane + H_2	100-200	10	"	
	5	5±0.7	Ditto	200-380	8	"	II. 1.142 ml of ordinary acetylene adsorbed; 54.6%
	6	1±0.2	"	400	4	"	
	7	0	"	485	5	"	III. 0.619 ml of labelled acetylene adsorbed; 28.2% of amount adsorbed, mean content of labelled acetylene 46%
	8	Not analyzed	"	500	2	"	
14	1	24± 1	Acetylene	Room	–	Desorption, 15 hrs.	Weight of catalyst 0.4796 g
	2	15± 1	Ethane + acetylene	Ditto	–	Hydrogenation 4 hrs	I. 0.92 ml of ordinary acetylene adsorbed; 20% saturation of surface
	3	28± 1	Ditto	"	–	Hydrogenation 15 hrs	II. 1.019 ml of labelled acetylene adsorbed; 22% of surface occupied
	4	8± 0.4	Acetylene	20-175	–	Heating, + H_2	III. 0.545 ml of ordinary acetylene adsorbed; 10% of surface occupied; mean content of labelled acetylene 41%
15	1	37±1.6	Acetylene	Room	–	Desorption	Catalyst from experiment 14 I. 1.37 ml of labelled acetylene adsorbed
	2	20±2	Ethane	Ditto	–	Hydrogenation	II. 0.224 ml of ordinary acetylene adsorbed; average content of labelled acetylene 85.8%

lower saturations methane is formed. Acetylene adsorbed on the most active centers, in the region of small saturations, undergoes a transformation as a result of which hydrogen is evolved on heating, and a carbide type of carbon-nickel bond is formed.

TABLE 2

Expt. No.	Sample No.	% Content of labelled acetylene carbon	Gas	Temp., °C	Method of removal	Conditions of adsorption of acetylene
6	1	25±2	Acetylene	Room	Desorption	Weight of catalyst 0.5 g
	2	13±0.6	Ethane	Ditto	Hydrogenation	I. 0.589 ml of labelled acetylene adsorbed; saturation of surface 12%
	3-4	Not analyzed		Room-100	Desorption	II. 0.196 ml of ordinary acetylene adsorbed; saturation of surface 4%
	5	27±9	Methane + H_2	350	Ditto	
	6	46±1.5	Ditto	450	"	Mean content of labelled acetylene 75%
7	1	14±0.8	Ethane	Room	Hydrogenation	Weight of catalyst 0.5 g
	2	11±1	Ditto	Ditto	Ditto	I. 0.365 ml of labelled acetylene adsorbed; saturation of surface 8%
	3	35±2	Methane	450	Desorption	II. 0.156 ml of ordinary acetylene adsorbed; saturation of surface 3%. Mean content of labelled acetylene 70%

Table 2 presents the results of two similar experiments, in one of which the catalyst was first dried in a stream of nitrogen before being introduced into the reaction vessel. The object of the experiments was to determine the order of magnitude of the activation energy of adsorption of acetylene at hydrogenation centers. The experiments were performed as described above. A 0.5 g sample of catalyst was placed in the reaction vessel, and was reduced with hydrogen before the experiment, at 450° in experiment 16, and at 300° in experiment 17, with subsequent degassing at the same temperatures. As appears in Table 2 it is the acetylene of the second portion which undergoes hydrogenation in both cases. The saturation of the surface is in these experiments much lower than in the preceding ones, in accordance with the lower adsorptive activity of the given specimen.

The experiments show that hydrogenation proceeds basically at active centers corresponding with a 12-16% saturation of the surface, and with an activation energy of 15-16 kg cal/mol, as found from adsorption measurements.

3. Discussion of results

The above-described experiments show that the active surfaces of the catalysts examined contain active centers which differ from each other in respect of their activation energies and heat of adsorption, as well as of their catalytic properties. We observed the following reactions of acetylene adsorbed on metallic nickel:

$$1.\ (C_2H_2)_{ads.} \longrightarrow C_2H_2$$

$$2.\ 4(C_2H_2)_{ads.} \longrightarrow 2CH_4 + (C_6)_{ads.}$$

$$3.\ (C_2H_2)_{ads.} \longrightarrow (C_2)_{ads.} + H_2$$

$$4.\ (C_2H_2)_{ads.} \xrightarrow{+H_2} C_2H_4$$

$$5.\ (C_2H_2)_{ads.} \xrightarrow{+2H_2} C_2H_6$$

The first three processes took place during desorption of acetylene at room temperature.

(a) Reversible adsorption of acetylene. When we adsorbed two portions of acetylene, of which one contained labelled carbon, we found that the first portion of acetylene desorbed at room temperature consisted of both portions, in various proportions. Successive portions desorbed at higher temperatures consist to an increasing extent of the second fraction of acetylene adsorbed. In experiment 13 the first fraction desorbed at room temperature contained 40% of the last adsorbed fraction of acetylene. The second portion, desorbed at 50-100°, contained 60±1% of this fraction. In experiment 14, the first portion desorbed at room temperature contained 76%, and the second, desorbed at 175°, 92% of the last adsorbed fraction of acetylene.

Thus desorption does not begin with the active centers of maximum $E_{ads.}$, at which adsorption takes place last, but with the more active centers, corresponding with lower saturation of the active surface. This is evidence of the complex nature of the relation between activation energy of adsorption and desorption. Fig. 2 represents one of the possible variants of the relation between $E_{ads.}$ and $E_{des.}$, explaining the effects observed.

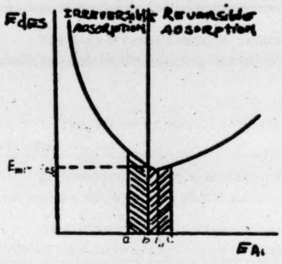


Fig. 2. Schematic representation of the relationship between energy of activation of desorption $E_{des.}$ and of adsorption $E_{ads.}$. Region a-b: methane forming centers; b-c hydrogenating centers.

The minimum activation energy of desorption corresponds with the value of activation energy E_0. At low levels of saturation, not attaining the minimum values of activation energy of desorption, desorption begins at the active centers having the maximum energies of activation of adsorption; at saturation levels exceeding this value desorption will, irrespective of the saturation level, take place first of all at the active centers for which the value of $E_{ads.} = E_0$. In the case of adsorption of two portions of acetylene, of which one is labelled with C^{14}, the ratio of labelled to ordinary acetylene in the desorbed gas will depend on how much of the active surface has been filled by the first portion, with relation to saturation corresponding with minimum values of activation energy of desorption. If the adsorption boundary between the two portions lies to the right of the saturation value corresponding with $E_{min.des.}$ then the first desorbed fraction will contain acetylene originating from the portion first adsorbed, while if to the left it will originate from the second portion. If the boundary lies close to the saturation value corresponding with $E_{min.des.}$, then the first and all succeeding desorbates will be made up of both adsorbed portions. In this, in view of the proportionality of $E_{ads.}$ to the logarithm of saturation (for an exponential type of function of distribution of active centers according to $E_{ads.}$), the content of acetylene derived from the last portion adsorbed will increase in successive desorbed fractions of acetylene; this was in fact confirmed by experiment.

The region of reversible adsorption on an active specimen is at a saturation of 45%. In experiment 12 the boundary between the first and the second portions adsorbed (of which the second contained labelled C^{14}) is at 45% saturation. The first fraction of the hydrogenation product, which usually differs little from the first desorbed product with respect to its C^{14} content, contains 57% of acetylene of the last portion adsorbed. It follows that the adsorption boundary between the two portions of acetylene is in this experiment close to the saturation value corresponding with minimum desorption activation energy values. Since the velocity of desorption is determined by the value of desorption activation energy, succeeding fractions of desorbed gas should contain acetylene from active centers of activation energy both higher and lower than E_0. However, irreversible adsorption takes place in the region of low activation energy; here the adsorbed acetylene either undergoes decomposition or enters into reaction faster than it can be desorbed from the surface. In view of this succeeding portions of desorbed gas will contain more of the acetylene which had been adsorbed on centers of high activation energy, i.e., more of the acetylene adsorbed from the second portion.

The acetylene desorbed at 120-150° in experiment 12 contains 96% of the acetylene from the second portion adsorbed. In experiment 14 the boundary of adsorption between succeeding portions is at 42% saturation, i.e., at a lower saturation than that corresponding with $E_{min.des.}$. Accordingly, the acetylene desorbed at room temperature contains 75% of acetylene from the last adsorbed portion, i.e., more than in experiment 12. The fraction desorbed at higher temperatures, up to 175° as in experiment 12, contains 92% of acetylene from the last adsorbed portion.

The experimental data thus agree with the assumed relationship between $E_{ads.}$ and $E_{des.}$. We have already encountered this type of relationship when studying the kinetics of desorption of activated adsorbed hydrogen on sugar charcoal [8]. In that case this character was even better defined, giving rise to a series of anomalies in the kinetics of desorption, and leading to appearance of "relictual zones" in adsorption on charcoal which had been partly degassed after adsorption thereon on hydrogen. We would add that such a connection between energy of activation of adsorption and desorption may occur when the distribution functions of active centers according to activation energies and heats of adsorption are not of the same type. This in turn requires that the linear relation postulated by certain authors between activation energy and heat of adsorption should not be present.

(b) Additional experiments were performed, dealing with the kinetics of hydrogenation and adsorption of acetylene, in order to establish whether the adsorptional mechanism of hydrogenation is basic to the process. This was shown to be the case, and a group of hydrogenating centers was found in the catalyst which determined the kinetics of the reaction. The results obtained from the study of the active surface by the differential isotope method, and from the kinetic study permit of the drawing of definite conclusions regarding the mechanism of formation of methane and of hydrogenation; these will be considered in the next paper.

The author has pleasure in expressing his gratitude to S. Z. Roginsky for his valuable advice, and for the interest he took in the carrying out of this research.

SUMMARY

1. The active surface of a nickel catalyst is not uniform with regard to activation energy of adsorption of acetylene.

2. Hydrogenation of acetylene takes place at certain of the centers which adsorb acetylene reversibly. These centers occupy 4-6% of the surface, at the boundary between reversible and irreversible adsorption.

Formation of methane takes place at active centers with higher heats of adsorption. Decomposition of acetylene with liberation of hydrogen takes place at the active centers with the highest heats of adsorption.

3. The non-linear nature of the relation between $E_{ads.}$ and $E_{des.}$ is established.

Received June 23, 1951

Institute of Physical Chemistry
Academy of Sciences USSR

LITERATURE CITED

[1] S. Z. Roginsky and O. M. Todes. Acta. Phys. Chim. USSR. 21, 519 (1946).

[2] N. P. Keier and S. Z. Roginsky. Proc. Acad. Sci. 57, 157 (1947).

[3] N. P. Keier and S. Z. Roginsky. Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 1, 27 (1950).

[4] N. P. Keier. Catalysis. Transactions All-Union Conference on Catalysis, Kiev. Publ. Acad. Sci. Ukrain. SSR, 1950.

[5] L. Maquenne, Ann. Chim. Phys. 28, 261 (1893).

[6] N. P. Keier and S. Z. Roginsky. Bull. Acad. Sci. USSR, Div. Chem. Sci. 96, 571 (1947).

[7] N. P. Keier. Proc. Acad. Sci. 72, 1071 (1950).

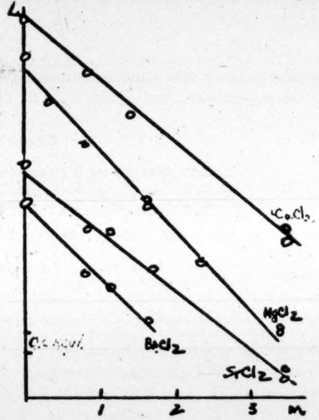
[8] N. P. Keier and S. Z. Roginsky, J. Phys. Chem. 23, 897 (1949).

COORDINATION NUMBERS OF THE IONS Mg^{2+}, Ca^{2+}, Sr^{2+}, AND Ba^{2+} IN AQUEOUS SOLUTIONS

O. Ya. Samoilov

It was thought to be of interest to extend to bivalent ions the results described in our previous paper [1] for univalent ions, and to determine the integral heats of dissolution of Mg, Ca, Sr, and Ba chlorides in aqueous HCl.

The salt $MgCl_2 \cdot 6H_2O$ was prepared by storing the commercial salt (analytically pure) in a desiccator over 68% sulfuric acid at 20°, to constant weight, which was usually achieved in about 6 weeks. Calcium, strontium, and barium chloride were taken in the anhydrous form; strontium and barium chloride (chemically pure) were dehydrated by heating their mixtures with chemically pure ammonium chloride (in order to avoid hydrolytic decomposition) until all the NH_4Cl was eliminated. Calcium chloride dihydrate was prepared similarly, and was dehydrated by melting in a platinum crucible.



Integral heats of dissolution of $MgCl_2$, $MgCl_2 \cdot 6H_2O$, $CaCl_2$, $SrCl_2$, and $BaCl_2$ in aqueous HCl

The amounts of the salts taken for the calorimetric experiments were such that the concentrations obtained (constant for each salt) were from 0.03 to 0.06 g mols. of salt per 50 g mols. of water. The integral heats of dissolution were measured in a calorimeter with an outer jacket maintained at a temperature of $25 \pm 0.01°$. The methods used in making the measurements were identical with those described in an earlier paper [2]. After weighing out samples of $MgCl_2 \cdot 6H_2O$ the tube with the salt was replaced in the desiccator for 2-3 days, until the weight became constant.

The results of determination of integral heats of dissolution are given in Table 1, and are represented in the graph. The concentration of acid m is expressed as g-mol. HCl per 50 g-mol. water, and the heat of dissolution L as kg.-cal per mole of salt. The curves are distributed along the ordinate axis (retaining the same scale). The heats of dissolution of $BaCl_2$ are given only up to a HCl concentration of 1.65, in view of the low solubility of this salt in hydrochloric acid. The various determinations of $\underline{L}$ were accurate to within 1% on the average; the low heats of dissolution of $MgCl_2 \cdot 6H_2O$ were an exception to this.

Table 2 gives the values of β (cal/mol 1 m) for the salts studied ($\beta = -\Delta L/\Delta m$; $\Delta L/\Delta m$ are derived from experimental results by the method of least squares).

Inasmuch as the ions under examination are bivalent the values of β should be halved, in order to find the coordination numbers from equations (2) or (3) [1]. If we write equation (2) for $CaCl_2$ as

$$K\left(\frac{2n_{Ca^{2+}}}{r_{Ca^{2+}} + 1.38} - \frac{2n_{Cl^-}}{r_{Cl^-} + 1.38}\right) = \beta; \qquad (1)$$

the figure 2 in the first term is connected with the charge of Ca^{2+}, and in the second term with the circumstance that each mole of the dissolved salts gives rise to two g-ions of Cl^-. If we divide equation (1) by 2 we see that the coordination number of bivalent ions is found in the same way as for univalent ions, with the difference that instead of β we take β/2.

TABLE 1

Integral heats of dissolution of salts in aqueous HCl at 25°

Dissolved salt	Concentration of HCl in moles per 50 moles water	Heat of dissolution in Kcal per mole of salt	Dissolved salt	Concentration of HCl in moles per 50 moles water	Heat of dissolution in Kcal per mole of salt
$MgCl \cdot 6H_2O$	0.00	+3.40	$CaCl_2$	3.51	+16.71
	0.32	+2.91		3.51	+16.86
	0.81	+2.45			
	1.63	+1.84			
	1.63	+1.78	$SrCl_2$	0.00	+11.82
	2.37	+1.19		0.84	+11.13
	3.40	+0.48		1.12	+11.09
	3.40	+0.43		1.68	+10.70
				3.46	+ 9.62
				3.46	+ 9.52
$CaCl_2$	0.00	+19.12			
	0.84	+18.54	$BaCl_2$	0.00	+ 2.84
	1.70	+18.09		0.81	+ 2.06
				1.12	+ 1.91
				1.65	+ 1.55*

---

* Measurements made with a second specimen of $BaCl_2$ gave values for L at this concentration equal to +1.71 and +1.72 Kcal /mole, but measurements relating to a single series were taken for the curve.

TABLE 2

Values of β for the salts studied

Salt	$MgCl_2$	$CaCl_2$	$SrCl_2$	$BaCl_2$
β	897	666	636	780

$$K\left(\frac{n_{Ca^{2+}}}{r_{Ca^{2+}} + 1.38} - \frac{n_{Cl^-}}{r_{Cl^-} + 1.38}\right) = \frac{\beta}{2} \quad . \qquad (1')$$

It should first of all be noted that the coordination number of Mg^{2+} in aqueous solutions is practically equal to that of the Li^+ ion; for $MgCl_2$ $\beta/2 = 448$, and for LiCl $\beta/2 = 465$ [1] (the values differ by about 4%). This appears to be connected with the equality of the coordination numbers in solution, and not simply with an equality of crystallochemical radii (electrostatic equivalence of Li^+ and $\frac{1}{2}\ MgCl^{2+}$).

The natural conclusion to be drawn from this is that the ions Li^+ and Mg^{2+} have a coordination number of 6 in aqueous solution; this is the maximum possible in connection with the relation of the radius of these ions to that of water molecules. It has, however, been shown [1] that the upper limit of possible values for the coordination number of the Li^+ ion is 4.23, so that this conclusion must be rejected.* Apparently the closeness of a number of properties of the Li^+ and Mg^{2+} ions in aqueous solution is responsible for the effect.

Taking $K = 1.17 \cdot 10^3$ and $n_{Cl^-} = 4.4$ [1] we can derive the coordination numbers of the ions Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} in aqueous solutions at 25° from the values of $\beta/2$. These numbers (n) are given in Table 3. The coordination numbers rise from the ion Mg^{2+} to the ion Ba^{2+}; we know that the energy of hydration of these ions falls in the same order. This shows the difference between coordination numbers of ions and their so-called hydration numbers. If, however, we calculate the surface density of packing of water molecules in the first coordination layer of the ions, ρ', suggested previously as an indicator of hydration [1], we see that the value of ρ' falls from Mg^{2+} to Ba^{2+}, although it remains greater than for water.** This is as could be expected, as we know that the given ions are hydrated.

TABLE 3

Coordination numbers in aqueous solution (n) and ρ' for the ions Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} at 25°

Ion	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
n	3.8	4.0	4.4	4.8
ρ'	0.065	0.054	0.050	0.048

---

* This is confirmed in the determination of the coordination number of the ion Be^{2+} in aqueous solutions.

** At 25° $\rho'_{H_2O} = 0.044\ \mathring{A}^{-2}$ [1].

As in the case of the ions Li^+, Na^+, K^+, Cl^-, Br^-, and I^-, examined in an earlier paper, the coordination numbers are close to the mean value for the coordination number of water molecules in water. It may be concluded that the structure of water determines the structure of dilute aqueous electrolyte solutions.

The modification by ions of the structure of water is connected, in the first place, with introduction into water of particles whose radius differs from that of water molecules, in the second place, with the difference between the coordination numbers of the ion and of water molecules (should such a difference be found), and in the third place with the re-ordering of the molecules of water closest to the ion. It is evident that of the factors enumerated the second is the most important energetically, inasmuch as the effect of the change in coordination number is exerted at a great distance. It appeared that only a very small change takes place in the coordination number, or possibly none at all.

Coordination numbers of the order of 6 could be peculiar to the ions, in accordance with their distribution in vacant positions of the structure of water. Such coordination numbers were not, however, encountered. This is as would be expected, if the re-orienting effect exerted by ions on surrounding molecules of water is taken into account; this re-orientation is of greater magnitude in vacancies in the structure of water, surrounded by 6 molecules of water, than in their absence. The structure of dilute solutions in which the ions are surrounded by water molecules represents the least modification of the structure of water.

The general conclusion drawn agrees with the results of roentgenographic examination of aqueous solutions of LiCl, LiBr, and RbBr as reported by Beck [3], who found that on the curves representing intensity of scattering of X-rays by solutions of LiBr or RbBr (concentrations 4.0 and 2.58 M, respectively) the peak due to scattering by pure water is the prevailing one. Since at these concentrations scattering due to the ions considerably exceeds that due to water, Beck draws the conclusion that the ions are arranged in these solutions similarly to water molecules, i.e., they are distributed in the structure of water in such a way that they "replace" its molecules. We cannot speak literally of the replacement by ions of water molecules; the ions modify the arrangement of the adjacent water molecules, and the relative orientation of molecules (orientation of tetrahedrally arranged negative and positive poles of the molecules) is the determining factor for the structure of water. It is scarcely permissible to draw any analogy with solid solutions, however. We would add that Bernal and Fowler [4] took the coordination number of bivalent ions as being 6, on the basis of calculation of the energy of coordination by ions of molecules of water in solutions; Eley and Evans [5] came to a similar conclusion.

According to Beck [3] the structure of very concentrated solutions (e.g., 13 M) of LiCl or LiBr is similar to that of the appropriate hydrated salt, i.e., the molecules of water are arranged together with the ions of which the salt structure is made up. Beck's conclusion is probably of general applicability, and Mathieu and Lounsbury [6] arrived at the same conclusion on the basis of a study of Raman spectra of concentrated aqueous nitrates.

The question arises in what way the transition between these two states takes place (structures of dilute and concentrated solutions). A continuous transition is possible [6]*; however, the work of Danilov and his co-workers has established the existence of a eutectic structure in a number of liquid solutions. Similarly, the study of scattering of X-rays by molten alloys which give eutectic phase diagrams has led to the conclusion that they contain groupings with the structures of both one and the other component [7]. The existence of such groupings has also been established in aqueous solutions of acetone [8]. It is evident that in a number of liquid systems consisting of the molecules A and B the combinations AA and BB may be more probable energetically than the combination AB [9].

Aqueous solutions of electrolytes may also, within certain ranges of temperature and concentration, possess a eutectic structure, in this meaning of the term. Depending on the temperature, the structure of solutions resembles one or another [illegible] of their components, as the concentration is increased (the structure of water in dilute, and of the solid hydrate in concentrated, solutions). These structures only gradually undergo deformation [10], and further change in concentration leads to the appearance of a eutectic structure.

A relationship of this sort appears to be suggested by the results of a study of the dependence on temperature of the intensity of scattering of X-rays by NaCl and LiCl solutions, of a composition close to the eutectic, reported by Danilov and Neimark [11], who found that at low temperatures the second maximum of the intensity of scattering curve for water, which is barely perceptible at room temperature, reappears. According to these authors this may be due to appearance of concentration inhomogeneities in the solutions at low temperatures, when those parts of it which gain water assume its structure.

---

* A continuous transition is achieved at excessively low temperatures.

SUMMARY

1. Integral heats of dissolution of $MgCl_2 \cdot 6H_2O$, $CaCl_2$, $SrCl_2$, and $BaCl_2$ in aqueous HCl of various concentrations, at 25°, have been determined in a calorimeter with an isothermic envelope.

2. Coordination numbers have been found, using the method previously described, for aqueous solutions of the ions Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}. The values are close to 4, and they rise from Mg^{2+} to Ba^{2+}. The mean density of distribution of water molecules around the ions diminishes from Mg^{2+} to Ba^{2+}.

3. The structure of dilute aqueous solutions of electrolytes is determined largely by the structure of water.

Received November 1, 1951

N. S. Kurnakov Institute of General and Inorganic Chemistry
Academy of Sciences USSR

LITERATURE CITED

[1] O. Ya. Samoilov, Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 3, 398, (1952).*

[2] A. F. Kapustinsky and O. Ya. Samoilov, Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 4, 337, (1950).

[3] J. Beck, Phys. Z., 40, 474, (1939).

[4] D. Bernal and R. Fowler, Advance in Phys. Sci., 14, 586, (1934).

[5] D. Eley, M. Evans, Trans. Faraday Soc., 34, 1093, (1938).

[6] J. P. Mathieu, M. Lounsbury, Comptes. rend. 229, 1315 (1949).

[7] V. I. Danilov and I. V. Radchenko, J. Exp. Theoret. Phys., 7, 1158, (1937).

[8] V. I. Danilov, A. M. Zubko, and A. I. Danilova, J. Exp. Theoret. Phys., 19, 243, (1949).

[9] V. I. Danilov, Bull. Acad. Sci. USSR, Phys. Series, 5, 30 (1941).

[10] G. W. Stewart, J. Chem. Phys. 7, 869 (1939).

[11] V. I. Danilov and V. E. Neimark, Phys. Z. Sow., 10, 673 (1936).

---

* See Consultants Bureau English Translation, p. 379.

STUDY OF SYSTEMS CONTAINING HYDROGEN PEROXIDE

PART 2. THERMAL PROPERTIES AND DEHYDRATION OF PERHYDRATES OF SODIUM CARBONATE

S. Z. Makarov and V. N. Chamova

It was shown in the preceding paper [1] that the following phases are formed in the system $Na_2CO_3-H_2O_2-H_2O$ at 0-20°: $Na_2CO_3 \cdot H_2O \cdot 1.5H_2O_2$; $Na_2CO_3 \cdot H_2O \cdot 2H_2O_2$ and $Na_2CO_3 \cdot 2H_2O_2$.

Specimens of these compounds were subjected to thermal analysis, with differential registration on a registering pyrometer of the N. S. Kurnakov type. The heating curve of $Na_2CO_3 \cdot H_2O \cdot 1.5H_2O_2$ (Fig. 1) shows two inflections, due to an endothermic effect at 105° and to an exothermic one at 120°. The endothermic effect corresponds with dehydration, with formation of the anhydrous perhydrate, and the exothermic one with decomposition of the anhydrous perhydrate, with evolution of oxygen.

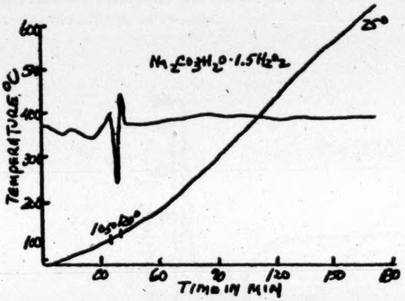


Fig. 1.

The results of analysis of the original substance and of the products of heating at 105-110° and at 120° are given in Table 1. We see that the process begins with dehydration, followed by decomposition of perhydrol of crystallization.

The heating curve of the compound $Na_2CO_3 \cdot H_2O \cdot 2H_2O_2$ (Fig 2) is similar, and shows an endothermic effect at 95°, and an exothermic one at 125°. The salt had initially the % composition:

Na_2CO_3	55.32
H_2O_2	36.38
H_2O	8.30

The nature of the heating curves indicates a means of obtaining anhydrous perhydrates of sodium carbonate from the corresponding hydrated salts, viz., by dehydrating at temperatures below the exothermic decomposition point. This also affords confirmation of our previously made conclusion regarding the perhydrate nature of the type of peroxide compounds.

TABLE 1

Substance	Content %		
	in original substance	at 105-110°	at 120°
Na_2CO_3	62.75	75.75	99.95
H_2O_2	30.32	22.14	–
H_2O	6.93	2.11	1.0

TABLE 2

Composition	Content %		
	Na_2CO_3	H_2O_2	H_2O
Original $Na_2CO_3 \cdot H_2O \cdot 1.5H_2O_2$	62.75	30.32	6.93
	60.57	29.15	10.28
Dehydrated $Na_2CO_3 \cdot 1.5H_2O_2$	68.18	32.30	–
Theoretical $Na_2CO_3 \cdot 1.5H_2O_2$	67.42	32.44	–
Original $Na_2CO_3 \cdot H_2O \cdot 2H_2O_2$	55.32	36.38	8.30
Dehydrated $Na_2CO_3 \cdot 2H_2O_2$	60.33	40.52	–
Theoretical $Na_2CO_3 \cdot 2H_2O_2$	61.00	39.00	–

We found that the compounds $Na_2CO_3 \cdot 1.5H_2O_2$ and $Na_2CO_3 \cdot 2H_2O_2$ were in fact obtained by heating the hydrates at appropriate temperatures, and at reduced pressures (8-10 mm).

The dehydrated perhydrate $Na_2CO_3 \cdot 2H_2O_2$ gives a sharply defined exothermic effect on the heating curve (Fig.3) at 50°, associated with evolution of oxygen, and gives a second, endothermic effect at 140°.

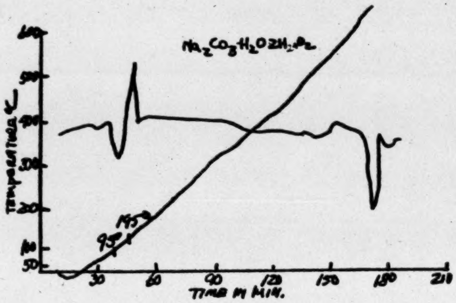


Fig. 2

SUMMARY

1. Heating curves with differential registration, using a registering pyrometer, are constructed for the perhydrates $Na_2CO_3 \cdot H_2O \cdot 1.5H_2O_2$ and $Na_2CO_3 \cdot H_2O \cdot 2H_2O_2$. The curves have two inflections, the first being due to an endothermic effect, associated with dehydration, and the second to an exothermic effect, due to thermal decomposition of perhydrate, with evolution of oxygen.

2. The anhydrous perhydrates $Na_2CO_3 \cdot 1.5H_2O_2$ and $Na_2CO_3 \cdot 2H_2O_2$ may readily be prepared from the hydrated salts obtained from sodium carbonate and aqueous perhydrol, by heating at temperatures below those of the exothermic effects, in vacuum.

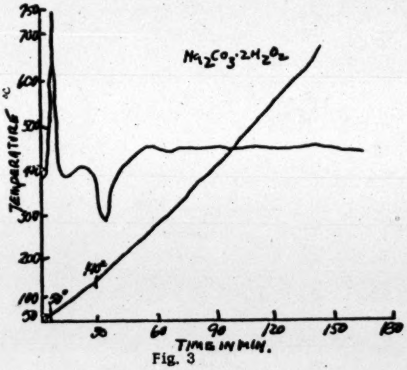


Fig. 3

Received January 4, 1952

Laboratory for Peroxide Compounds
Academy of Sciences USSR

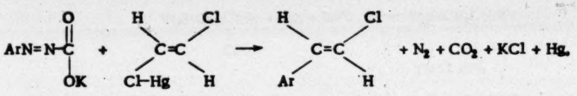
LITERATURE CITED

[1] S. Z. Makarov and V. N. Chamova, Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 3, 255 (1951).

MECHANISM OF REACTION OF MAGNESIUM ALKYL HALIDES WITH β-SILICOALKYL HALIDES*

A. D. Petrov and V. F. Mironov

β-Silicoalkyl halides $(\mathrm{-\overset{|}{\underset{|}{Si}}-C-C-X})$ closely resemble, as regards their structure and chemical behavior, the β-halides of a series of organometallic halides (M–C–C–X), of which a detailed study has been made by Nesmeyanov and co-workers [1]. These authors showed that a typical member of this series, Biginelli's complex (ClHgCH=CHCl), may undergo decomposition when treated with certain reagents, such as C_6H_5MgBr, to give acetylene and mercuric chloride, from which it was prepared, while in other cases the acetylene of the complex reacts with the reagents forming new C–C bonds. The following reaction illustrates this:



$$\mathrm{ArN{=}N{-}C({=}O)OK + ClHgCH{=}CHCl \longrightarrow ArCH{=}CHCl} + N_2 + CO_2 + KCl + Hg.$$

This reaction enables us to synthesize the formerly difficultly preparable cis- ω-chlorostyrenes. The metal, in this case mercury, is eliminated, and is not present in the reaction product. Reactions are, however, also known in which the metal remains attached to the product, but this is usually found for reactions affecting the halogen atom attached to the metal, and not in the β-position with respect to it. An example is given by the reaction described by the Indian scientist [2]:

$$Cl_2AsCH{=}CHCl + 2PhMgBr \longrightarrow Ph_2As(CH{=}CHCl) + 2MgBrCl.$$

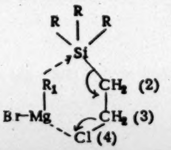
We were able to find the conditions under which β-silicoalkyl halides only partly undergo decomposition, the main reaction being with the halogen in the β-position to the silicon, by the general scheme:

$$\mathrm{{\geq}Si{-}C{-}C{-}X + RMgX \longrightarrow {\geq}Si{-}C{-}C{-}R.}$$

This opens up new perspectives for the synthesis of silicohydrocarbons and of silicon-organic compounds in general. The majority of the silicohydrocarbons now known were prepared by the Wurtz or the Grignard-Wurtz reaction from silicoalkyl halides in which the halogen is attached to the silicon atom. Silicoalkyl halides in which the halogen atom is in the α-, β-, or γ-position to the silicon have only recently become known. The first β-silicoalkyl halide was β-chloroethyltriethylsilane, $(C_2H_5)_3SiCH_2CH_2Cl$, prepared in 1937 by Ushakov and Itenberg [3], who also showed that it differs sharply from α-halides in its instability in dilute aqueous alkalis. Whitmore and co-workers [4], in studying the reactions and properties of β-silicoalkyl halides, in the cases of certain primary β-chlorides, found that they underwent cleavage of the Si–C bonds when taken for the Grignard-Wurtz synthesis:

$$Cl_3SiCH_2CH_2Cl + 4EtMgBr \longrightarrow CH_2{=}CH_2 + Et_4Si + 4MgBrCl.$$

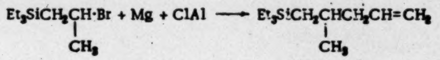
They represented the mechanism of cleavage at the Si–C bonds, the so-called β-decomposition, as a cyclic process, proceeding in the six-membered coordination complex:



---

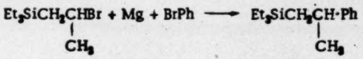
[*] A lecture given at a general meeting of the Division of Chemical Sciences of the Academy of Sciences USSR, on March 28, 1952.

In this complex the Si atom and the radical R_1 of the Grignard reagent are in the 1-6 positions. The Si atom attracts an electron pair belonging to the radical R_1, and at the same time transposition of the electrons of the 2nd and 3rd carbon atoms takes place. The process leads to formation of a new R_1–Si bond, with simultaneous formation of MgX_2 and ethylene. The work of these American scientists has led to the acceptance of the view that β-silicoalkyl halides are quite useless as intermediates for syntheses, in particular for those based on the Grignard-Wurtz reaction. Thus, for example, Sommer and Marans [5] draw attention in a paper published in 1950, to the instability of compounds containing halogen, hydroxyl, or other functional groups in the β-position, and they recommend the use of compounds with the functional group at a greater distance from the Si, such as the γ-position. In arriving at these aprioristic assumptions the American authors neglected to take into consideration the structure of either the β-silicoalkyl halide or of the compounds with which it reacts, and greatly overemphasized the importance of the β-influence. We have shown in two of our papers [6] that these authors were unduly pessimistic regarding the synthetic possibilities of β-silicoalkyl halides. In the first of these papers we described the reactions:


(1)

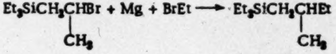
$$Et_3SiCH_2\underset{CH_3}{CH}{\cdot}Br + Mg + ClAl \longrightarrow Et_3SiCH_2\underset{CH_3}{CH}CH_2CH{=}CH_2 \quad (1)$$

Yield 43 %


(2)

$$Et_3SiCH_2\underset{CH_3}{CH}Br + Mg + BrPh \longrightarrow Et_3SiCH_2\underset{CH_3}{CH}{\cdot}Ph \quad (2)$$

Yield 22%


(3)

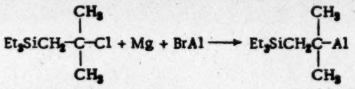
$$Et_3SiCH_2\underset{CH_3}{CH}Br + Mg + BrEt \longrightarrow Et_3SiCH_2\underset{CH_3}{CH}Et \quad (3)$$

Yield 17%

It was possible to carry out these reactions because the β-silicoalkyl halides, which are highly sensitive to thermal factors, were prepared and stored at low temperatures until they were taken for the reactions. A study of the behavior of β-silicoalkyl halides in a number of different reactions showed that whether or not β-decomposition or synthesis takes place at a C–X bond depends on a number of factors. In the first place, the direction in which the reaction proceeds depends on the nature of the RMgX compound used. Active magnesium alkyl or aryl halides (allyl, phenyl) favor the transfer of the whole reaction to the C–X bond, whereas in the cases of BrMgEt or BrMgMe the reaction takes place at both the C–X and the Si–C bonds. But the direction of the reaction also depends on the nature of the halogen-containing group in the β-position to the silicon atom; secondary β-silicoalkyl halides are more resistant to β-decomposition than are primary ones, and it was later found that tertiary ones are even more resistant.

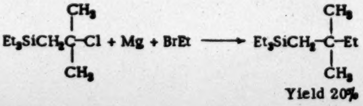
In our second paper we studied the effect of the nature of the halogen, and also investigated the reactions of various Grignard reagents with tertiary and primary β-silicoalkyl halides. It was found that the use for the syntheses of secondary β-chlorosilanes instead of the corresponding β-bromides gave yields 1.5 times greater.

Attempts to prepare the tertiary β-bromide or β-iodide by adding HBr or HI to $Et_3SiCH_2\underset{CH_3}{C}{=}CH_2$ at 70° were unsuccessful, but the chloride was obtained similarly, by addition of HCl. This chloride reacted with RMgX, where R is allyl or ethyl (some β-decomposition in the latter case):



$$Et_3SiCH_2{-}\overset{CH_3}{\underset{CH_3}{C}}{-}Cl + Mg + BrAl \longrightarrow Et_3SiCH_2\overset{CH_3}{\underset{CH_3}{C}}{-}Al$$

Yield 30%



$$Et_3SiCH_2\overset{CH_3}{\underset{CH_3}{C}}{-}Cl + Mg + BrEt \longrightarrow Et_3SiCH_2{-}\overset{CH_3}{\underset{CH_3}{C}}{-}Et$$

Yield 20%

We then added HBr to $Et_3SiCH{=}CH_2$, and condensed the primary β-bromide so obtained with MgBrAl or MgBrEt:

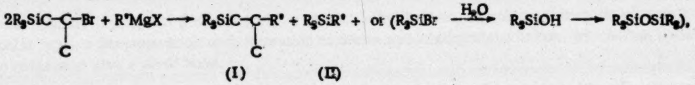
$$Et_3SiCH_2CH_2Br + Mg + BrAl \longrightarrow \underset{\text{Yield 24\%}}{Et_3SiCH_2CH_2Al}$$

$$Et_3SiCH_2{-}CH_2Br + Mg + BrEt \longrightarrow Et_3SiCH_2CH_2Et + Et_4Si.$$

In the latter case only traces of triethylbutylsilane were obtained, the main product being Et_4Si, by β-decomposition.

Having investigated the effect of the nature of the Grignard reagent and of the halogen-containing radical on the strength of the Si–C bond and of transfer of reactivity to the C–X bond, we next studied the effect of the radicals attached to the Si atom. With this object we decided to prepare a series of trialkyl- (and arylalkyl)-allylsilanes R_3SiAl, and to study the reactions of the β-bromides prepared therefrom with Grignard reagents, in order to find in which cases the reaction of synthesis prevails, and in which the dominating reaction is that of β-decomposition.

In this way, for the reaction which for secondary β-silicoalkyl bromides may be represented by the equations:



$$2R_3SiC{-}\underset{\displaystyle C}{\underset{|}{C}}{-}Br + R'MgX \longrightarrow \underset{(I)}{R_3SiC{-}\underset{\displaystyle C}{\underset{|}{C}}{-}R'} + \underset{(II)}{R_3SiR'} + \text{ or } (R_3SiBr \xrightarrow{H_2O} R_3SiOH \longrightarrow R_3SiOSiR_3),$$

we have to find the ratio of (I) to (II) in the products. The following 7 allylsilanes were prepared: Ph_3SiAl, $Ph_2MeSiAl$, $PhMe_2SiAl$, Me_3SiAl, Et_3SiAl, Pr_3SiAl and Bu_3SiAl; the yields were about 50% when the radicals attached to the Si atoms contained an odd number of carbon atoms, and about 80% when this number was even.

TABLE 1

Yields of $R_3SiCH_2CH(CH_3)R'$, as % calculated on initial $R_3SiCH_2CH{=}CH_2$

R \ R'	Et	Pr	Ph	Al
$PhMe_2$	5	–	–	24
Me_3	5	6	9	35
Et_3	12	25	23	50
Pr_3	12	20	–	38
Bu_3	20	–	–	50

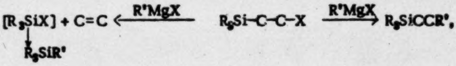
We were not able to perform any syntheses with the first of these allylsilanes, owing to the readiness with which it polymerizes. β-Bromopropyltrialkylsilanes were prepared from the remaining 6 trialkyl (or triarylalkyl-)-silanes, in the usual way, at −70°. The β-bromides were added to a 2-3 fold excess of R'MgX. The reaction with allyl bromide was conducted according to Yavorsky. The results of the syntheses are presented in Table 1, from which it appears that the yields of alkylsilanes are 2-4 times greater for β-bromides with a $SiEt_3$ group than with a $SiMe_3$ group. Moreover, partial β-decomposition is here observed even with AlMgBr, which does not cause β-decomposition of even the least stable primary β-bromide (in the case of $Et_3SiCH_2CH_2Br$). The smaller yield of silanes from trimethyl- than from triethyl-β-bromopropylsilane suggests that β-decomposition results not so much from thermal instability of the β-silicoalkyl halides, as the first of these halides is considerably more heat resistant than is the second, as from the reactivity of the C–X bond (determined by the influence of all the atoms entering into the β-silicoalkyl halide). Evidence supporting the view that thermal stability should be distinguished from chemical stability of β-silicoalkyl halides is also to be found in the literature.

Thus it is evident from the work of Whitmore et al [7] that $Cl_3SiC{-}C{-}Cl$ can be distilled without decomposition at 152°, whereas $Et_3SiC{-}C{-}Cl$ decomposes at 80° [4]. Yet the former compound reacts instantaneously with 0.1 N alkali, with evolution of ethylene, while the latter reacts only very slowly. Whitmore interprets these facts as showing that β-decomposition is due to action of nucleophilic OH^- on the Si atom, and further that replacement of one chlorine atom attached to Si by R causes a ten-fold lowering of β-decomposition due to OH^-, since the presence of electronegative substituents on the Si atom renders it a more effective center of nucleophilic action [8]. It is evident that a similar effect applies to the reactions studied by us. With diminishing electronegativity of the series of radicals attached to Si

$$C_6H_5{-} > CH_3{-} > C_2H_5{-} > C_3H_7{-} > C_4H_9{-}$$

the yields of silanes obtained by condensation at the C–X bonds rise, and β-decomposition diminishes. To this we should add an additional small correction, depending on whether the radicals attached to Si have an odd or even number of carbon atoms; this affects not only the yield of trialkylallylsilanes, but also that of silanes prepared from β-silicoalkyl halides. It may also readily be foreseen that such factors as steric hindrance, which has scarcely been studied, can also affect the yields of silicohydrocarbons.

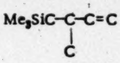
We found, further, that if to EtMgBr we add $Et_3SiC-\underset{\substack{|\\ C}}{C}-Br$, and very soon after we decompose the product by adding water, without boiling, we obtain, in addition to $Et_3Si-C-\underset{\substack{|\\ C}}{C}-Et$ obtained by the Grignard-Wurtz reaction, the silanol Et_3SiOH; Et_4Si, the final product of β-decomposition, is practically absent. When, however, the reaction product is subjected to prolonged boiling, silanol is not produced, the by-product being Et_4Si. It is evident that Et_4Si is formed from Et_3SiBr and EtMgBr. When the time of boiling is too short Et_3SiBr does not afford Et_4Si, giving silanol instead. These observations, which were not noted by Whitmore, show that the mechanism of β-decomposition suggested by him is erroneous. The reactions of β-decomposition and of synthesis from β-silicoalkyl halides can more reasonably be represented by the following simple mechanism:



$$\underset{\substack{\downarrow\\ R_3SiR'}}{[R_3SiX]} + C{=}C \xleftarrow{R'MgX} R_3Si-C-C-X \xrightarrow{R'MgX} R_3SiCCR',$$

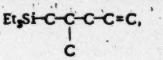
showing that the primary reaction of β-decomposition of silicoalkyl halides, as well as of metallo-organic compounds of similar type, is decomposition with formation of olefin and trialkylsilane halide, which then condenses with Grignard reagent to give a Si–R' bond.

We then prepared the as yet unknown δ-silicoalkyl bromides from the β-bromides. HBr adds on slowly to the appropriate silico-olefins [in particular to compound (II)]



$$Me_3SiC-\underset{\substack{|\\ C}}{C}-C{=}C$$

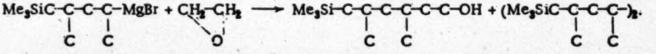
(I)



$$Et_3Si-C-\underset{\substack{|\\ C}}{C}-C-C{=}C,$$

(II)

but the yields of δ-silicoalkyl bromides were 90 and 84%, respectively. In distinction to the β-bromides they were weakly ionized compounds, not giving a precipitate with boiling aqueous $AgNO_3$, and reacting with NaOH somewhat similarly to α-silicoalkyl halides or to primary alkyl halides. Ethylene oxide reacted with one of these reagents as follows:

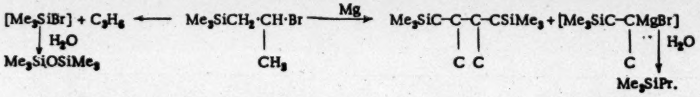


$$Me_3SiC-\underset{\substack{|\\ C}}{C}-C-\underset{\substack{|\\ C}}{C}-MgBr + \underset{\diagdown O \diagup}{CH_2-CH_2} \longrightarrow Me_3Si-C-\underset{\substack{|\\ C}}{C}-C-\underset{\substack{|\\ C}}{C}-C-C-OH + (Me_3SiC-\underset{\substack{|\\ C}}{C}-C-\underset{\substack{|\\ C}}{C}-)_2.$$

The yield of alcohol was 37%.

It is of interest that α- and γ-silicoalkyl halides react with Mg and then with ethylene oxide to give only the corresponding alcohols. The β-bromides not only react readily with Grignard reagents, but they are also able themselves to afford such reagents, although with considerable β-decomposition and evolution of olefins.

The extent of β-decomposition may be somewhat reduced by preparing the Grignard reagents from β-silicoalkyl halides at low temperatures. The reaction proceeded as follows:



$$\underset{\substack{\downarrow H_2O\\ Me_3SiOSiMe_3}}{[Me_3SiBr]} + C_3H_6 \longleftarrow Me_3SiCH_2\cdot\underset{\substack{|\\ CH_3}}{CH}\cdot Br \xrightarrow{Mg} \underset{(I)}{Me_3SiC-\underset{\substack{|\\ C}}{C}-\underset{\substack{|\\ C}}{C}-CSiMe_3} + \underset{(II)}{\underset{\substack{\downarrow H_2O\\ Me_3SiPr.}}{[Me_3SiC-\underset{\substack{|\\ C}}{C}MgBr]}}$$

In view of the thermal stability of the β-silicoalkyl halide taken, its β-decomposition at room temperature might be explained as being due to activation of the decomposition reaction by the Grignard reagent formed. Compounds (I) and (II), which show that the β-silicoalkyl halide forms a Grignard reagent, were isolated after treating the product with water and removing the products of β-decomposition (hexamethyldisiloxane) with concentrated sulfuric acid.

A certain similarity between β- and δ-silicoalkyl halides, which differ so sharply in their thermal and chemical stability, may consist in the tendency of both of them to afford disilanes. The formation of Grignard reagents by β-silicoalkyl halides may permit of the use of the latter for the synthesis of alcohols, at least, by condensation with certain carbonyl compounds.

EXPERIMENTAL

Phenylallyldimethylsilane $C_6H_5(CH_3)_2SiCH_2CH=CH_2$ (I). A few ml of allyl bromide is added to 54 g of magnesium (2.2 moles) in 1 liter of absolute ether, contained in a 2 l. flask fitted with a reflux condenser, a stirrer, and a dropping funnel. The stirrer is switched on when reaction begins, and a mixture of 171 g of phenyldimethylsilyl chloride (1 mole) (b.p. 194.4°/750 mm; n_D^{20} 1.5080; d_4^{20} 1.0307] and 133 g of allyl bromide (1.1 mole) is added gradually during 7 hrs. The ether is distilled off during 2-3 hrs on the following day, and the solid residue is heated at 100° for 7 hrs. The ether which had been distilled off is returned to the flask, the contents of which are treated first with water, and then with a minimum amount of 10% HCl. The ethereal extract is dried with Na_2SO_4, the ether is distilled off and the liquid residue is fractionated, using a column with 10-15 theoretical plates, giving 144 g of phenylallyldimethylsilane, b.p. 213.6°/751 mm; n_D^{20} 1.5090; d_4^{20} 0.8911; MR_D 59.07; calculated [11] MR_D 58.89, yield 81.7%.

Found %: H 9.16; 9.17; C 75.24; 74.97; Si 15.97; 16.29
$C_{11}H_{16}Si$. Calculated %: H 9.15; C 74.94; Si 15.92

Other allylsilanes were prepared similarly.

Diphenylallylmethylsilane $(C_6H_5)_2CH_3SiCH_2CH=CH_2$ (II), b.p. 310-311°/740 mm; n_D^{20} 1.5660; d_4^{20} 0.9876; MR_D 78.73; calculated MR_D 78.71. Yield 50%.

Found %: H 7.66; C 79.96; Si 11.07
$C_{16}H_{18}Si$. Calculated %: H 7.62; C 80.62; Si 11.77.

Allyltrimethylsilane $(CH_3)_3SiCH_2CH=CH_2$ (III). This product has been described by Sommer [9]. Me_3SiAl was, similarly to $PhMe_2SiAl$, prepared by Yavorsky's method. The use of this method is not only simpler, but it also gives higher yields, which are 8% greater than those obtained by the method involving separate preparation of AlMgX. Allyltrimethylsilane has b.p. 85.4°/750 mm; n_D^{20} 1.4075; d_4^{20} 0.7195. Yield 59%.

Allyltripropylsilane $(CH_3CH_2CH_2)_3SiCH_2CH=CH_2$ (IV); b.p. 217°/748 mm; n_D^{20} 1.4490; d_4^{20} 0.7950; MR_D 66.93; calculated MR_D 66.85. Yield 51%.

Found %: H 13.28; C 72.28: Si 13.83
$C_{12}H_{26}Si$. Calculated %: H 13.21; C 72.64: Si 14.14

Allyltributylsilane $(CH_3CH_2CH_2CH_2)_3SiCH_2CH=CH_2$ (V). This has been described by Petrov and Shchukovsky; it has b.p. 252.3°/750 mm; n_D^{20} 1.4515.

Triallylpropylsilane $CH_3CH_2CH_2Si(CH_2CH=CH_2)_3$ (VI): b.p. 218.3°/750 mm; n_D^{20} 1.4705; d_4^{20} 0.8178; MR_D 66.37; calculated MR_D 65.91. Yield 36.6%.

Found %: H 11.66; C 74.14; Si 13.88
$C_{12}H_{22}Si$. Calculated %: H 11.41; C 74.15; Si 14.44

Phenyltriallylsilane $C_6H_5Si(CH_2CH=CH_2)_3$ (VII): b.p 274.8°; (751) n_D^{20} 1.5300; d_4^{20} 0.9174; MR_D 76.90; calculated MR_D 76.47.

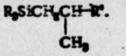
Found %: H 9.14; C 78.95
$C_{15}H_{20}Si$ Calculated %: H 8.83; C 78.88

β-Bromopropyltrialkylsilanes $R_3SiCH_2CH(CH_3)Br$. These were obtained in the usual way [6], by bubbling HBr through compounds (I), (II), (III), (IV), and (V) at −70°. The β-bromides obtained from compounds I and V were very viscous oils. The β-bromides were not purified, but were taken directly for the reactions; the β-chloride obtained from compound (III) and HCl was, however, first purified.

β-Chloropropyltrimethylsilane $(CH_3)_3SiCH_2CH(CH_3)Cl$ (VIII): b.p. 43-46°(25) n_D^{20} 1.4280; d_4^{20} 0.8738; MR_D 44.37; calculated MR_D 44.38.

Found %: Cl 23.64
$C_6H_{15}SiCl$. Calculated %: Cl 23.53

β-Alkylpropyltrialkylsilanes (trialkyl-2-methylalkylsilanes) $R_3SiCH_2CH(CH_3)-R'$.



$$R_3SiCH_2\underset{CH_3}{\underset{|}{C}H}-R'$$

The β-bromides were added to a 2-3 fold excess of R'MgX, which was prepared in the usual way from the appropriate R'X and Mg; the amount of β-bromide taken varied from 0.15 to 0.3 moles, and it was added at −70°. The reaction with allyl bromide was conducted according to Yavorsky, and it was possible, during the addition of β-bromide to R'MgX, to estimate the extent of β-decomposition from the amount of propylene evolved. After adding the β-bromide the mixture was boiled for 5-8 hrs, after which the ether was in some cases distilled off and the solid residue was heated on a boiling water bath, in order to convert the β-decomposition product R_3SiBr into R_3SiR'. Otherwise, during the subsequent decomposition with water, formation of the corresponding silanols R_3SiOH and disiloxans $R_3SiOSiR_3$ takes place, and these products interfere with the purification of the main product. After treatment with water, drying, and distilling off the ether, the residue is fractionally distilled. In preparing saturated silicohydrocarbons the residue was first extracted with concentrated sulfuric acid. The yields and properties of the products are presented in Tables 1 and 2.

The new silicohydrocarbons Pr_3SiEt and Bu_3SiEt were obtained incidentally to the preparation of compounds (7) and (10). The corresponding R_3SiR' or R_3SiOH and $R_3SiOSiR_3$ compounds were formed as a result of β-decomposition in the other cases, except for compounds (8), (9), and (11), where there was apparently no β-decomposition.

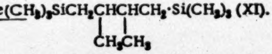
Ethyltripropylsilane $(CH_3CH_2CH_2)_3SiC_2H_5$ (IX): b.p. 207-210°(748); n_D^{20} 1.4375; d_4^{20} 0.7824; MR_D 62.47; calculated MR_D 62.69.

Found %: H 13.98; C 70.32; Si 14.66
$C_{11}H_{26}Si$. Calculated %: H 14.06; C 70.88; Si 15.06

Ethyltributylsilane $(CH_3CH_2CH_2CH_2)_3SiC_2H_5$ (X): b.p. 252-254°(740); n_D^{20} 1.4445; d_4^{20} 0.7942; MR_D 76.49; calculated MR_D 76.58.

Found %: Si 12.22
$C_{14}H_{32}Si$. Calculated %: Si 12.28

1.4-Di-(trimethylsilyl)-2,3-dimethylbutane $(CH_3)_3SiCH_2CHCHCH_2\cdot Si(CH_3)_3$ (XI).

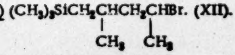


$$(CH_3)_3SiCH_2\underset{CH_3}{\underset{|}{C}H}\underset{CH_3}{\underset{|}{C}H}CH_2\cdot Si(CH_3)_3$$

Compound (III) and HBr give 71.5 g (0.366 moles) of trimethyl-β-bromopropylsilane, a few ml of which is added to 20 g (0.824 moles) of magnesium powder in 250 ml of ether, contained in a 500 ml flask. A violent exothermic reaction at once begins, and the mixture becomes black. The β-bromide is added during 90 min., with energetic stirring, and maintaining the temperature at 10-15° (evolution of gas is considerable at 20-25°, and at the b.p. of ether the yields of silicohydrocarbons are less than a half of those at 10-15°). The contents of the flask are treated with water on the following day, the ethereal layer is separated, and the ether is distilled off. The residue is treated with concentrated sulfuric acid, and the acid layer is poured into water, when hexamethyldisiloxane separates. The product not extracted by sulfuric acid is washed with water, dried, and fractionally distilled, to yield 3.2 g of trimethylpropylsilane [10] b.p. 88°/730 mm; n_D^{20} 1.3929; d_4^{20} 0.7027 and 5.2 g of a substance of b.p. 218-220.5°; this was 1,4-di-(trimethylsilyl)-2,3-dimethylbutane, b.p. 220-220.3°/730 mm; n_D^{20} 1.4400; d_4^{20} 0.7922; MR_D 76.68; calculated MR_D 76.95. Yield 12.3%.

Found %: H 13.04; C 62.69; Si 23.48
$C_{12}H_{30}Si_2$. Calculated %: H 13.12; C 62.53; Si 24.35

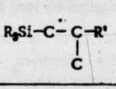
Trimethyl-4-bromo-2-methylpentylsilane (δ-bromide) $(CH_3)_3SiCH_2CHCH_2CHBr$. (XII).



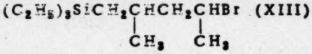
$$(CH_3)_3SiCH_2\underset{CH_3}{\underset{|}{C}H}CH_2\underset{CH_3}{\underset{|}{C}H}Br$$

HBr is passed through 18.7 g (0.17 moles) of trimethyl-2-methylbut-3-enylsilane (see Table 2), cooling in a freezing mixture containing dry ice, and continuing the reaction until the theoretical gain in weight is achieved. The temperature of the mixture is then allowed to rise to room temperature, when considerable amounts of HBr are evolved; the product is for this reason again cooled and saturated with HBr at −70°, and this treatment is repeated until the gain in weight at 20° corresponds with the theoretical. Fractionation of the product gave 25.5 g of trimethyl-4-bromo-2-methylpentylsilane, b.p. 92-93°/18 mm; n_D^{20} 1.4590; d_4^{20} 1.0628; MR_D 61.02; calculated MR_D 61.11. Yield 90%.

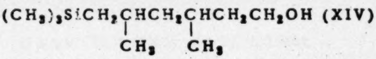
TABLE 2

New Silicohydrocarbons of the type  $R_3Si{-}C{-}\overset{\bullet}{C}(C){-}R'$

No.	Formula	R	R'	B.p. °C	D mm	n_D^{20}	d_4^{20}	MR_D found	MR_D calc.	M	Calculated % C	Calculated % H	Calculated % Si	Found % C	Found % H	Found % Si
1	$C_{13}H_{22}Si$	PhMe$_2$	Et	242	735	1.4895	0.8806	67.70	68.62	206.37	75.66	10.75	13.60	–	–	13.4
2	$C_{14}H_{22}Si$	PhMe$_2$	Al	256-8	743	1.4990	0.8859	72.38	72.00	218.38	76.99	10.15	12.85	–	–	12.21
3	$C_8H_{20}Si$	Me$_3$	Et	133.2	747	1.4120	0.7369	48.72	48.80	144.3	66.58	13.97	19.45	66.41	13.96	19.20
4	$C_9H_{22}Si$	"	Pr	154.5	750	1.4190	0.7492	53.37	53.43	158.33	68.27	14.01	17.72	68.58	14.02	–
5	$C_{12}H_{20}Si$	"	Ph	221-3	745	1.4940	0.8792	63.69	63.78	192.34	74.93	10.48	14.59	75.70	10.37	13.75
6	$C_9H_{20}Si$	"	Al	151.3	750	1.4264	0.7575	52.91	52.96	156.31	69.15	12.90	17.95	69.18	12.82	–
7	$C_{14}H_{32}Si$	Pr$_3$	Et	240-3	745	1.4450	0.7965	76.54	76.58	228.46	73.60	14.12	12.28	73.64	14.00	12.42
8	$C_{15}H_{34}Si$	"	Pr	257-9	750	1.4470	0.8011	80.87	81.21	242.48	74.29	14.13	11.57	74.50	14.14	11.21
9	$C_{15}H_{32}Si$	"	Al	255-6	760	1.4545	0.8098	80.49	80.74	240.47	74.92	13.41	11.67	74.99	13.10	–
10	$C_{17}H_{38}Si$	Bu$_3$	Et	272-4	740	1.4480	0.8010	90.41	90.47	270.53	75.47	14.16	10.37	–	–	10.99
11	$C_{18}H_{38}Si$	"	Al	288-9	745	1.4568	0.8122	94.70	94.84	282.54	76.51	13.56	9.93	76.60	13.69	9.56

Triethyl-4-bromo-2-methylpentylsilane  $(C_2H_5)_3SiCH_2\underset{CH_3}{C}HCH_2\underset{CH_3}{C}HBr$ (XIII)

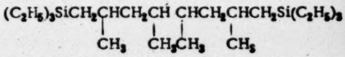
This was prepared similarly to the preceding δ-bromide from triethyl-2-methylbut-3-enylsilane [6], and had b.p. 124°/8 mm., n_D^{20} 1.4745; d_4^{20} 1.0517; MR_D 74.70; calculated MR_D 75.00. Yield 84%.

6-Trimethylsilyl-3.5-dimethylhexanol  $(CH_3)_3SiCH_2\underset{CH_3}{C}HCH_2\underset{CH_3}{C}HCH_2CH_2OH$ (XIV)

The Grignard reagent was prepared from 22 g of the δ-bromide (XII) (0.093 moles) and 2.5 g of magnesium (0.103 moles) in 100 ml of ether; the reaction proceeds energetically, and after its completion the mixture is boiled for 2 hours, after which 11 g of ethylene oxide (0.25 moles) and 150 ml of ether are added. The contents of the flask, which had set to a jelly by the next day, were left for 8 days, and were then treated with water. Fractional distillation of the dried ethereal layer gave 7 g of the alcohol (XIV), b.p. 120-125°/5 mm., n_D^{20} 1.4480; d_4^{20} 0.8315; MR_D 65.16; calculated MR_D 64.24. Yield 37.2%.

Found %: Si 14.78; 15.31. $C_{11}H_{26}SiO$. Calculated %: Si 13.87.

The results both of elementary analysis and of OH group determination by Tserevitinov's method (83%) suggested contamination of the product with a silicohydrocarbon, and a substance which was insoluble in concentrated H_2SO_4, b.p. about 300°, n_D^{20} 1.4510, was found in the higher b.p. fractions. We considered this to be a silicohydrocarbon produced by a Wurtz condensation of the δ-bromide, as in the case of reaction (XI) for the β-bromide. This supposition was confirmed by the results of the next experiment.

1,8-Di-(triethylsilyl)-2,4,5,7-tetramethyloctane (XV)  $(C_2H_5)_3SiCH_2\underset{CH_3}{C}HCH_2\underset{CH_3}{C}H\,\underset{CH_3}{C}HCH_2\underset{CH_3}{C}HCH_2Si(C_2H_5)_3$

18 g of the δ-bromide (XIII) (0.066 moles) is added to 1.6 g of Mg powder (0.066 moles) in 50 ml of ether. After completion of the reaction, initiated by addition of a crystal of iodine, the reaction mixture is boiled for 5 hours, and is then treated with water and 10% HCl. The ether is distilled off, and the residue is treated with concentrated H_2SO_4. The residue insoluble in H_2SO_4 consists of 3 g of triethyl-2-methylpentylsilane [6], b.p. 222-226°, n_D^{20} 1.4436, and 7 g of compound (XV), b.p. about 380°, n_D^{20} 1.4687; d_4^{20} 0.8443; MR_D 131.5; calculated MR_D 132.4.

Found %: H 13.64; C 72.62; Si 13.69; $C_{24}H_{54}Si_2$. Calculated %: H 13.65; C 72.27; Si 14.08.

The fraction soluble in H_2SO_4 was recovered by pouring the solution into water; it consists of about 1 g of hexaethyldisiloxane, and about 2 g of higher b.p. fractions.

The analyses were performed in the Microanalysis Laboratory, Institute of Organic Chemistry, Academy of Sciences U.S.S.R.

SUMMARY

1. Contrary to the views of American workers, it has been shown that β-silicoalkyl halides may be used for the synthesis of silicohydrocarbons by the Grignard-Wurtz reaction; this is illustrated by the synthesis of 12

silicohydrocarbons, in yields of 20-50% (not counting a large number of syntheses with smaller yields).

2. A mechanism is advanced for the so-called β-decomposition of β-silicoalkyl halides ($R_3Si-C-C-X$). This consists of liberation of an olefin molecule, with attachment of the β-halogen atom to the silicon. The reaction may proceed spontaneously, at temperatures of from +50° to -50°, according to the structure of the silicoalkyl halide, or it may be activated by the Grignard reagents. The Grignard reagents R'MgX react simultaneously both with the product of β-decomposition R_3SiX and with the β-silicoalkyl halides, the yields of silicohydro carbons (products of β-decomposition or of synthesis) varying widely according to the nature of R and R'.

3. It is shown that the amount of β-decomposition falls in the series primary → secondary → tertiary silicoalkyl halides, and is greater for bromides than for chlorides. The radical R also affects the results, the yield of decomposition products falling, and of synthesis products rising, in the order C_6H_5, CH_3, C_2H_5, C_3H_7, C_4H_9, i.e., in order of diminishing electronegativity of the radicals. The extent of β-decomposition could in some cases be reduced by conducting the syntheses at low temperature.

LITERATURE CITED

[1] K.A. Kocheshkov, I.F. Lutsenko, and O.A. Reutov. Prog. Chem., 18, 497 (1949).

[2] Das Gupta H. N. Y., Ind. Chem. Soc., 14, 231 (1937); C.A. 7, 423 (1937).

[3] S. N. Ushakov and A. M. Itenberg. J. Gen. Chem., 7, 2495 (1937).

[4] L. H. Sommer, G. M. Goldberg, E. Dorfman, F. C. Whitmore, J. Am. Chem. Soc., 68, 1083 (1946), L. H. Sommer, D. L. Bailey, F. C. Whitmore, ibid 70, 2869 (1948).

[5] L. H. Sommer, N. S. Marans, ibid 72, 1935 (1950).

[6] A. D. Petrov and V. F. Mironov. Proc. Acad. Sci., U.S.S.R., 75, 5,(1950), and 80, 5,(1951).

[7] L. H. Sommer, F. C. Whitmore, J. Am. Chem. Soc. 68, 485 (1946).

[8] L. H. Sommer, R. E. Van-Strein, F. C. Whitmore, ibid 71, 3056 (1949).

[9] L. H. Sommer, L. Y. Tyler, F. C. Whitmore, ibid 70, 2872 (1948).

[10] F. C. Whitmore, L. Sommer, ibid 68, 475 (1946).

[11] E. L. Warrick, ibid 68, 2456 (1946).

Received March 28, 1952

Institute of Organic Chemistry, Academy of Sciences U.S.S.R.
D. I. Mendeleev Moscow Institute for Chemical Technology

CATALYTIC ALKYLATION OF AMMONIA WITH HALOGEN DERIVATIVES OF ALKANES AND CYCLANES

PART 2. EFFECT OF THE NATURE OF THE HALOGEN AND OF ITS POSITION IN THE MOLECULE ON AMINATION OF ALKYL HALIDES

V. A. Nekrasova and N. I. Shuikin

We know from the literature of the problem of amination of alkyl halides [1] that the most suitable for liquid phase amination are chloro- and bromo-derivatives. We thought it of interest to investigate the behavior of halides of aliphatic and alicyclic hydrocarbons in conditions of catalytic amination in the vapor phase.

Our experiments showed that the nature of the halogen, and its position in the chain significantly affect the results. We made a comparative study of amination of chloro-, bromo-, and iodo-ethane, 1-chloro-2-methylpropane, 1-bromo-2-methylpropane, 1-chlorooctane, and 1-bromooctane, at a catalyst based on magnesium oxide. The volume of catalyst was in all cases 100 ml, and the molecular ratio of ammonia to organic halide was 2:1. The experiments lasted 1 hour, at 310°, at a rate of flow of 0.2 (volume velocity). The properties of the halides taken are given in Table 1, and the experimental results are presented in Table 2.

TABLE 1
Properties of the Alkyl Halides Taken

Alkyl halide	B.p. °C (corr.)	n_D^{20}	d_4^{20}
Chloroethane	12.5	–	0.9170 (d_6^6)
Bromoethane	38.5 (753 mm)	1.4238	1.4553
Iodoethane	72.5	1.5168	1.9132 (d_0^{20})
1-Chlorobutane	78.5	1.4015	0.8840
1-Bromobutane	101.0	1.4358	1.2689
1-Iodobutane	131.0	1.5000	1.6160
1-Chlorooctane	184.0	1.4425	0.8969
1-Bromooctane	201.5	1.4525	1.1078

The experiments showed that variations in the position of the halogen atom have a considerable effect on the yields, but that isomerism of the hydrocarbon chain was practically without effect; the results for 1-chlorobutane, 1-chloro-2-methylpropane, 2-chlorobutane, 2-chloro-2-methylpropane, 1-chlorohexane, 2-chlorohexane, 1-chloropentane, 2-chloropentane, 1-chlorooctane, and 2-chlorooctane are given in Tables 2 and 3. Primary chloroalkanes give a higher yield of amines than do secondary ones; thus the catalyzate from 1-chlorobutane contains 11.4 % of amino-nitrogen, as compared with only 8.6% from 2-chlorobutane. Comparison of amination of 1-chlorobutane and 1-chloro-2-methylpropane shows that isomerism of the hydrocarbon chain has little effect, the amino-nitrogen contents of the catalyzates being 11.4 and 10.9% respectively.

TABLE 2
Dependence of Yield of Amines on the Nature of the Halogen

Alkyl halide	Yield of condensate, as % of initial alkyl halide	% Amino-nitrogen content of catalyzate
Chloroethane	85.0	12.9
Bromoethane	80.0	9.9
Iodoethane	32.9	6.7
1-Chlorobutane	85.2	11.4
1-Bromobutane	78.8	9.5
1-Iodobutane	35.4	4.9
1-Chlorooctane	85.1	10.5
1-Bromooctane	80.3	9.1

We next studied vapor phase amination of alicyclic halides, at 340°, other conditions being as above. The results, given in Table 4, show that the same effects are found as for alkanes. The aminonitrogen content of the catalyzates from chloro- and bromocyclohexane is 11.9 and 10.7% respectively.

SUMMARY

1. The conditions for vapor phase contact catalytic amination of halogen derivatives of aliphatic and alicyclic hydrocarbons have been studied.

TABLE 3

Dependence of Yield of Amines on the Position of the Halogen in the Molecule

Chloroalkane	Yield of condensate, as % of initial alkane chloride	% Amino-nitrogen content of the catalyzate
1-Chlorobutane	86.5	11.4
1-Chloro-2-methylpropane	80.1	10.9
2-Chlorobutane	79.2	8.6
2-Chloro-2-methylpropane	78.7	5.6
1-Chlorohexane	82.1	12.0
2-Chlorohexane	79.1	10.1
1-Chloropentane	84.1	11.8
2-Chloropentane	79.2	9.1
1-Chlorooctane	83.2	10.5
2-Chlorooctane	80.1	9.1

TABLE 4

Synthesis of alicyclic amines in the vapor phase, as a magnesium oxide catalyst

Halogen derivative	Yield of condensate, as % of initial halogen derivative	% Amino-nitrogen content of the catalyzate
Chlorocyclopentane	98.1	11.5
Chlorocyclohexane	97.7	11.9
Bromocyclohexane	97.5	10.7

2. The nature of the halogen significantly affects the yields obtained which are higher for chloro- than for bromo-derivatives, and are lowest for iodo-derivatives.

3. The position of the halogen atom in the hydrocarbon chains significantly affects the yields, which are highest for primary alkyl halides.

4. Chlorine derivatives of alicyclic hydrocarbons give higher yields of amines than do bromine derivatives.

LITERATURE CITED

[1] N. I. Sheverdina and K. A. Kocheshkov. J. Gen. Chem. 8, 1825 (1938); E. Chablay, C. r. 156, 327 (1913); R. Norris Shreve and L. W. Rothenberger, Ind. Eng. Chem. 29, 1361 (1937).

Received April 3, 1952

Institute of Organic Chemistry
Academy of Sciences U.S.S.R.

ROLE OF OXYGEN-CONTAINING COMPOUNDS IN THE SYNTHESIS OF HYDROCARBONS FROM CARBON MONOXIDE AND HYDROGEN

Yu. B. Kagan, Yu. B. Kryukov, E. V. Kamzolkina, and A. N. Bashkirov

INTRODUCTION

It is generally known that the products of synthesis of hydrocarbons from carbon monoxide and hydrogen, discovered by Orlov [1], always contain a small amount of oxygen-containing organic compounds. This has given rise to the hypothesis [2] that oxygen-containing substances are intermediates in the synthesis of hydrocarbons; this view has had the support of a number of workers [3,4], but has had no further experimental confirmation. Eidus [5] studied the behavior of some of the simplest oxygen-containing compounds (formic acid, methanol, and ethanol) at Co catalysts of synthesis of hydrocarbons at 180-200°, at atmospheric pressure. He found that hydrocarbon synthesis is inhibited by addition of the oxygen-containing substances, showing that they cannot be regarded as intermediates in this synthesis.

New experimental material has, however, recently afforded fresh support for the hypothesis of intermediate formation of oxygen-containing products. In particular the possibility of achieving synthesis of alcohols and hydrocarbons at one and the same iron catalyst at different temperatures has been demonstrated [6]. The chief products of the reaction at low temperatures (190-200°) are alcohols, while at high temperatures (320-330°) the products are hydrocarbons. Storch [6] hence concludes that alcohols should be regarded as intermediate products in the synthesis of hydrocarbons, obtained therefrom by dehydration. Hall [7] attempted to confirm this view experimentally, and showed that with six-fold increase of velocity of flow of the gas the alcohol content of the product rises from 1.1 to 1.8% and that lowering of the reaction temperature at a cobalt catalyst also leads to increase in the yield of alcohols. This author [7] further studied the behavior of n-propanol and n-octanol at the catalysts Co-ThO_2-MgO-kieselguhr (100:6:3:200) and Fe-Cu-CaO-kieselguhr (100:5:10:30) in a stream of hydrogen, nitrogen and water gas, at the temperatures of the synthesis.

The author found that the amounts of unreacted alcohols varied, from 0 to 72% but, as the author himself admits [7], the products were not studied sufficiently. All that we know of them is that "on the basis of preliminary studies the chief products obtained at 150° appear to be water and the corresponding olefin and paraffin". Apart from these, propanol, at the same temperature, gave a liquid product of high b.p., which was not further examined, and octanol, at higher temperatures (183°), gave gaseous hydrocarbons and liquid products which boiled over a wide range of temperatures. Hall [7] draws the conclusion from these results that dehydration of the alcohols takes place, with production of olefins and for this reason he considers that alcohols may be intermediate products in the synthesis of hydrocarbons.

It seems to us, however, that these experimental results do not support such a view of the mechanism of the reaction. It should be stressed, in the first place, that it is impossible to draw conclusions regarding the nature and direction of the processes taking place unless we know the composition of the products obtained. It is also significant that when the experiments were performed under the conditions of the synthesis of hydrocarbons (in a stream of CO + H_2) the least conversion of alcohols was obtained. This fact is not in accord with the view that alcohols are intermediate products in the process of synthesis of hydrocarbons.

The results obtained by Hall in a single experiment involving variation in the rate of flow are also not conclusive, firstly because the absolute amount of alcohols in the reaction products is small, and secondly because with increase in the rate of flow the increase in the yield of alcohols is paralleled by increase in the yield of olefins. The experimental material presented below was obtained by us in connection with the study of the behavior of certain alcohols under the conditions of synthesis of hydrocarbons from carbon monoxide and hydrogen; it is in contradiction to Hall's view that hydrocarbons are formed from intermediate oxygen-containing compounds.

EXPERIMENTAL

The experiments were conducted in continuous action apparatus, working under pressure. The reactor in which the catalyst was placed was a steel tube, embedded in an aluminum block, the internal diameter of the tube being 14 mm. Our earlier papers [8, 9] give a description of the apparatus and method applied, and of the way in which the experimental data were evaluated. The apparatus was provided with a dropper, placed between the meter registering rate of flow of gas for synthesis and the reactor. A system of valves permitted the dropper to be included in the system without interrupting the reaction. An iron-containing catalyst was used. The initial gas contained carbon monoxide and hydrogen, in the proportion 1:1. The temperature applied was 300°, and the pressure was 20 atm.

BEHAVIOR OF n-BUTANOL UNDER SYNTHESIS CONDITIONS

n-Butanol, b.p. 117.3-117.8°, n_D^{20} 1,3991; d_4^{20} 0.8103, was introduced into the stream of CO–H by means of the dropping funnel. It had been shown previously that the catalyst is highly active, and that synthesis of hydrocarbons proceeds normally, with practically complete conversion of the carbon monoxide. The experiment lasted for 6 hours, during which time 34.5 g of n-butanol was added, and 32.5 g of liquid products were collected, together with 0.5 ml of gasoline vapor and 700 ml of "Gasol" in the absorber. Synthesis of hydrocarbons continued under the given conditions, although at a much slower rate.

The hydroxyl number of the condensate was 232, the ester number 138, and the acid number 4. The liquid reaction products (25.36 g) were subjected to detailed examination; the results of fractional distillation and analysis are presented in Table 1.

TABLE 1

Results of Fractional Distillation and of Analysis of the Product Obtained when n-Butanol is Added to the Synthesis Gas Mixture

B.p. of fraction, °C	Weight of fraction, g	% content of aldehydes	Weight of aldehydes, g	Acid number	Weight of acids, g	Hydroxyl number	Wt. of alcohols, g	Ester number	Weight of esters, g
40- 60	0.45	–	–	–	–	–	–	–	–
60- 80	1.40	6.7	0.09	0	0	–	–	–	–
80-110	7.17	9.2	0.66	0	0	260	2.46	0	0
110-125	5.46	1.6	0.09	0	0	670	4.83	41.9	0.59
125-158	1.95	0	0	5.25	0.016	345	0.89	210	1.05
158-168	7.36	0	0	7.1	0.080	0	0	379	7.18
Residue and losses	1.57	–	–	–	–	–	–	–	–
Weight of product	25.36	3.3	0.84	–	0.096	–	8.18	–	8.82

NOTE: The amount of oxygenous compounds was calculated on the basis of the data cited below.

The data of Table 1 show that the product obtained is clearly not homogenous. Its fractional composition, the distribution of the ester numbers among the fractions, and, in particular, the very high ester number of the fraction of b.p. 158-168°, show that the product consists basically of esters. A certain amount of acids are also formed, mostly in the fraction boiling at 158-168°, and of aldehydes, concentrated mostly in the fraction boiling at 80-110°.

The distribution of hydroxyl numbers through all the fractions suggests that the alcohol present in the catalyzate is unreacted n-butanol. The structure of the ester and aldehyde obtained were the subject of a special study.

STRUCTURE OF THE ESTER

Acids were eliminated from the fraction of b.p. 158-168°, and the residue was distilled, collecting the fraction of b.p. 165-167° (2.92 g). The constants of the fraction are given in Table 2.

The comparison of constants suggests that the ester is n-butyl n-butyrate.

TABLE 2
Constants of the Fraction of b.p. 165-167°

	Boiling point, °C	d_{20}^{20}	n_D^{20}	Ester number
Found	165-167	0.8694	1.4088	387.5
Published values for n-butyl n-butyrate [10]	166.4	0.872	1.4049	388.7

The whole of the fraction of b.p. 158-168° was hydrolyzed, and the resulting alcohol (1 g), b.p. 116-118°, d_4^{20} 0.8109; n_D^{20} 1.3984, was collected. The m.p. of the phenylurethane prepared therefrom, and recrystallized from petroleum ether, was 60°, and it did not give any depression with the phenylurethane of n-butanol. According to the literature, n-butanol has b.p. 117.7°, d_4^{20} 0.810; n_D^{20} 1.3993 [11], m.p. of phenylurethane 61°. The alcohol derived from hydrolysis of the ester is thus definitely shown to be n-butanol.

The salt of the organic acid present in the alkaline hydrolyzate was decomposed with 15% H_2SO_4, and the solution was extracted with ether, giving 2.5 g of a product boiling at 162-163.5°, which is the b.p. of n-butyric acid. The acid was definitely identified from its physical constants and acid number, and from the m.p. of its amide and the results of analysis of its silver salt.

TABLE 3
Constants of the Acid Obtained by Hydrolysis of the Fraction of b.p. 158 168°

	Boiling point, °C	d_4^{20}	n_D^{20}	Acid number	Melting point of amide, °C
Found	162-163.2	0.9564	1.3982	616.2	114.5-115
Published values for n-butyric acid [10]	163.5	0.9590	1.3979	636.5	115

The amide gave no m.p. depression with n-butyramide. The silver content of the silver salt of the acid was determined.

Found %: Ag 55.48. $C_4H_7O_2Ag$. Calculated %: Ag 55.34.

The ester was thus definitively identified as n-butyl n-butyrate.

IDENTIFICATION OF THE ALDEHYDE

A hydrochloric acid solution of 2:4-dinitrophenylhydrazine was added to the fraction of b.p. 80-110°, to give the 2:4-dinitrophenylhydrazone of the aldehyde contained in this fraction; after recrystallization from ethanol it melted at 121-122°. According to the literature [13] the m.p. of the 2:4-dinitrophenylhydrazone of n-butyraldehyde is 122°. The mixed m.p. shows no depression. It may hence be accepted that the aldehyde obtained is n-butyraldehyde.

The elucidation of the structure of the reaction products allows of their determination in the catalyzate (see Table 1). From the above values for hydroxyl, acid, and ester numbers, together with other data from Table 1, we obtain the following reaction balance:

n-Butanol introduced into the reaction	34.5 g
Found in the catalyzate:	
n-Butanol	10.60 g
Butyl butyrate, n-butyraldehyde, and n-butyric acid	12.63 g
Other liquid and gaseous products	10.67 g
Total	33.90 g

It is evident from this balance that of 34.5 g of n-butanol taken in the reaction 23.2 g was found in the catalyzate, in the form of unreacted alcohol and of its oxygenous conversion products. Even if we assume that the whole of the remaining n-butanol has undergone conversion into hydrocarbons it is evident that oxygen-containing products are greatly in excess of hydrocarbon products. It would follow that if n-butanol is an intermediate product in the synthesis of hydrocarbons from carbon monoxide and hydrogen we should expect to find an excess of oxygen-containing products in the catalyzate; this, however, is in contradiction to all the known experimental facts relating to the product of synthesis at an iron-containing catalyst under the given experimental conditions. This shows, therefore, that n-butanol cannot be regarded as an intermediate product of the synthesis of hydrocarbons from carbon monoxide and hydrogen.

The behavior of n-butanol was also studied under conditions of synthesis of hydrocarbons at atmospheric pressure. We used a typical alkali-activated precipitated iron-copper catalyst. The experiments were performed at 240°, using 1:1 CO—H_2 mixtures, passed through the catalyst at a volume velocity of about 100 hr^{-1}. The gas mixture contained, apart from the carbon monoxide and hydrogen, about 3% of n-butanol vapor. The fractional composition and the analytical data for the reaction product are given in Table 4.

TABLE 4

Characterization of the Product Obtained when n-Butanol is added to the Reaction Gas at Atmospheric Pressure

Boiling point of fraction, °C	% Content of fraction in product	Acid number	Hydroxyl number	Ester number	% Content of aldehyde (C_4H_8O) in the fraction
Up to 100	16.9	–	–	–	35.6
100-130	34.2	1.67	720	30.8	–
130-170	15.3	33.9	182	229.3	0
Solid residue	33.6	–	–	–	–

The values given in Table 4 show that n-butanol undergoes the same conversions under conditions of synthesis at atmospheric pressure as in the earlier experiments at higher pressures.

BEHAVIOR OF N-PROPANOL UNDER CONDITIONS OF SYNTHESIS

n-Propanol, b.p.96.6—97.0°; d_4^{20} 0.8039; n_D^{20} 1.3853, was introduced into the reactor in the way described above. The catalyst was first tested for 10 days with only CO—H mixture, at 300°/20 atm., and was found to be highly active. The productivity of the whole of the catalyst volume, with a rate of flow of the gas of 30 l. per hour, was about 4 g of hydrocarbon per hour, with 90% conversion of the carbon monoxide. In experiments with n-propanol the alcohol was added at a rate approximately equal to that of production of hydrocarbon, as found in the preliminary experiments, but the rate of delivery of the gas was reduced to a third, so that a considerable part of the catalyst surface remained free.

TABLE 5

Rate of supply of gas for synthesis, in l/hr.	% Contraction	% Conversion	Yield of hydrocarbons, ml/hr	
			Liquid	Gaseous
10	59	89.4	0.98	310

At this reduced rate of delivery of the initial gas hydrocarbon synthesis (before addition of propanol) was as shown in Table 5.

27 g of propanol was placed in the dropping funnel, and was delivered to the reactor during 9.5 hour This gave 34.26 g of liquid products, and 4000 ml of gaseous hydrocarbons, i.e., 1100 ml more than is obtained during the same time under ordinary conditions. The percentage composition of the initial gas and of that obtained from it 4.5 hours after addition of alcohol were as follows:

Gas	CO_2	C_nH_m	CO	H_2	CH_4
Initial	–	–	47.0	53.0	–
Final	43.3	5.7	4.3	43.2	3.6

Applying the formula proposed by certain of us [9] for the calculation of contraction:

$$K = \frac{3a_1 + 2b_1 - c_1 - d_1}{3a_2 + 2b_2 - c_2 - d_2},$$

where a_1, b_1, c_1 and d_1 are the CO_2, CO, H_2 and CH_4 contents of the gas initially and a_2, b_2, c_2 and d_2 are the corresponding values in the issuing gas, we find a value for contraction of 57.6% (experimental value 59.0%).

Applying the method of calculation earlier described [9], we obtain the following reaction balance:

1 cu. m. of the initial gas contains	470 l CO + 530 l H_2	
0.424 cu. m. of the final gas contains	19 l CO + 194 l H_2	
Total entering into reaction	451 l CO + 336 l H_2	
Of the reacted gas:		
Converted into CO_2	194 l CO	
Converted into H_2O		63 l H_2
Converted into CH_4	16 l CO	32 l H_2
Converted into higher hydrocarbons (C_nH_{2n})	241 l CO	241 l H_2

Expressed gravimetrically:	gC	gH	gO
The reacted gas contains	242.0	30.0	322.2
The CO_2 obtained contains	104.0	–	278.0
The H_2O obtained contains	–	5.6	45.0
The CH_4 obtained contains	8.6	2.9	–
The higher hydrocarbons obtained contain	129.0	21.5	–
The reaction products obtained contain	241.6	30.0	323.0

As is evident from these values, the synthesis of hydrocarbons proceeds with the same speed when n-propanol is introduced, and the degree of conversion of CO achieves 96%.

The liquid reaction products were next examined. The liquid was fractionated, and the aldehyde content and hydroxyl, acid, and ester numbers were determined for each fraction (see Table 6).

The calculation of the content of oxygen-containing compounds is based on the assumption that the process of conversion of n-propanol proceeds analogously to that of n-butanol. The data of Table 6 show that the amount of unreacted alcohol exceeds 50%. The total amount of oxygen-containing products of conversion of n-propanol is at least 4.4 g., and of liquid hydrocarbons not more than 10-11 g.

Under the given conditions, synthesis from carbon monoxide and hydrogen should during 9.5 hr. have given rise to about 7 g of liquid and at least 2900 ml of gaseous hydrocarbons (see Table 5). Even if we assume that all the remaining liquid and gaseous hydrocarbon products of the reaction resulted from conversion of n-propanol, the amount of hydrocarbons so formed would be approximately equal to that of oxygen-containing products actually obtained from n-propanol.

TABLE 6

Characterization of the Products Obtained when n-Propanol is added to the Reaction Gas

Boiling point of fraction, °C	Weight of fraction, g	% Content of aldehydes	Aldehyde content, g	Hydroxyl number	Alcohol content g	Acid number	Content of acids, g	Ester number	Ester content g
45-70	1.4	26.5	0.37	–	–	–	–	–	–
70-95	19.65	6.5	1.30	533	11.20	0.5	–	50.5	2.04
95-150	2.5	–	–	665	1.77	40.0	0.13	75	0.39
Residue	3.5	–	–	–	–	–	–	–	–
Losses	4.2	–	–	–	–	–	–	–	–
Reaction	3.0	3.6	0.11	200	0.64	–	–	–	–
For the whole of the product	34.25	–	1.78	–	13.61	–	0.13	–	2.43

Note: Fractional distillation was conducted from a Favorsky flask.

This fact, and also the relatively low degree of conversion of alcohol under conditions in which a considerable part of the synthetically active surface remains unoccupied, and in which practically total conversion of carbon monoxide takes place, show that n-propanol can also not be regarded as an intermediate product in the synthesis of hydrocarbons from carbon monoxide and hydrogen.

DISCUSSION OF THE RESULTS OBTAINED

The experimental material presented above showed that neither n-butanol nor n-propanol can be considered as intermediate products in the synthesis of hydrocarbons. These researches showed, moreover, that at the iron catalyst, under the given conditions, an ester-producing condensation of n-butanol and n-propanol takes place.

$$2C_4H_9OH \rightarrow C_3H_7COOC_4H_9 + 2H_2 \qquad (I)$$

$$2C_3H_7OH \rightarrow C_2H_5COOC_3H_7 + 2H_2 \qquad (II)$$

This condensation has been investigated in detail by numerous authors. The following mechanism seems, from a study of the literature [14, 15, 16], to be the most probable. It involved the three successive processes:

$$C_4H_9OH \rightarrow C_3H_7CHO + H_2 \qquad (III)$$

$$C_3H_7CHO + H_2O \rightarrow C_3H_7COOH + H_2 \qquad (IV)$$

$$C_3H_7COOH + C_4H_9OH \rightarrow C_3H_7COOC_4H_9 + H_2O \qquad (V)$$

The composition of the reaction product obtained in our experiments agrees well with this scheme [equations (III), (IV) and (V)].

It is significant that of these conversions the first two, (III) and (IV) are oxidation reactions, the oxidizing agent in reaction (IV) being water. This is of particular interest in view of our earlier finding [8, 17, 18] that the iron catalysts are able, under conditions of hydrocarbon synthesis from carbon monoxide and hydrogen, to catalyze the reaction of oxidation of carbon monoxide with steam, suggesting that these catalysts may have the general property of accelerating reactions of oxidation by water.

Their catalytic powers are not, however, limited to these reactions. Equation (III) points to the dehydrogenating activity of these catalysts under conditions of hydrocarbon synthesis. The property, reported in this and in earlier papers [8, 17, 18], of iron catalysts of hydrocarbon synthesis to accelerate different oxidation reactions should be regarded as one of their most important properties, emerging from the indissoluble unity of reactions of oxidation and reduction.

From this viewpoint it seems quite probable that the various oxygen-containing by-products of the process of synthesis of hydrocarbons are formed as a result of oxidation-reduction reactions of any oxygen-containing synthesis products, which are primary products in relation to other oxygen-containing products. Such a primary product of the side-reaction might, for example, be an aldehyde, formed from the appropriate olefins and CO + + H_2. Objections to such a mechanism might be based on the widely held view [7] that such reactions are not promoted by iron catalysts, and that the result of such reactions should be the formation in approximately equal amount of n- and iso-aldehydes and alcohols.

A paper has, however, appeared recently [19], reporting that a catalytic reaction may be achieved in the presence of iron carbonyl and isocarbonyl between olefins , carbon monoxide, and hydrogen, leading to formation of normal alcohols, without any admixture of iso-alcohols. This supports the view that the reaction proceeds as we postulate above.

SUMMARY

1. It has been shown that alcohols cannot be considered to be intermediate compounds in the synthesis of hydrocarbons.

2. It has been shown that iron catalysts of the synthesis of hydrocarbons are capable under the conditions of the synthesis reaction of accelerating the reactions of oxidation of alcohols and aldehydes.

3. Hypotheses regarding the possible mechanism of formation of the various oxygen-containing by-products of the reaction of synthesis of hydrocarbons are advanced.

Received February 16, 1952

Petroleum Institute
Academy of Sciences USSR

LITERATURE CITED

[1] E. I. Orlov, J. Russ. Chem. Soc., 40, 1142, 1588,(1908).

[2] O. C. Elvins, A. W. Nash, Nature ,18, 154,(1926).

[3] D. F. Smith, C. O. Howk, R. L. Golden, J. Am. Chem. Soc., 52, 3221 (1930).

[4] E. N. Firsanova, Chemistry of Solid Fuels 8, 892,(1937).

[5] Ya. T. Eidus, Bull. Acad. Sci. USSR, Div. Chem. Sci.,1, 65,(1943).

[6] H. H. Storch, Chem. Eng. Progress,44, 469 (1948).

[7] C. C. Hall, Ind. Chem. ,25, 163 (1949).

[8] A. N. Bashkirov, Yu. B. Kryukov, Yu. B. Kagan, and I. V. Kalechits, Proc. Petroleum Inst. Acad. Sci. USSR, 1, No. II, 306,(1950).

[9] Yu. B. Kryukov and A. N. Bashkirov, Proc. Petroleum Inst. Acad. Sci.,USSR, 2,(1952).

[10] T. E. Tables of Phys.-Chem. Tech. Constants 1, 219, Sov. Encycl. . Press, Moscow, (1927).

[11] M. H. Fournier, Bull. Soc. chim. France,7, 23,(1910).

[12] J. A. Mitschell, E. E. Reid, J. Am. Chem. Soc., 53, 1881 (1931).

[13] Ch. Allen, J. Am. Chem. Soc.,52, 2957 (1930).

[14] S. L. Lelchuk and M. V. Veltistova, Problems of Organic Chemistry, 4, 245, (1937).

[15] S. L. Lelchuk, M. V. Veltistova, and E. Ya. Gavrilova, Problems of Organic Chemistry, 5, 287 (1938).

[16] D. N. Vaskevich, Thesis, Moscow, 1946.

[17] A. N. Bashkirov, Yu. B. Kryukov, and Yu. B. Kagan, Proc. Acad.Sci., USSR, 67, 1029 (1940).

[18] A. N. Bashkirov, Yu. B. Kagan and Yu. B. Kryukov, Proc. Acad. Sci., USSR, 78, 275 (1951).

[19] J. W. Reppe, Acetylene Chemistry, New York.1949.

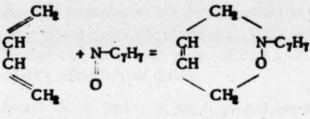
REACTIONS OF DIENE HYDROCARBONS WITH NITROSO-COMPOUNDS

ADDITION OF BUTA-1,3-DIENE TO p-NITROSOTOLUENE

Yu. A. Arbuzov

The results of a study of the reaction of nitrosobenzene with buta-1,3-diene [1,2] showed that addition takes place according to the diene synthesis, with production of 2-phenyl-3,6-dihydro-orthoxazine, the structure of which was derived from a study of the structure of its reduction products.

The results of a study of the reaction of addition of buta-1,3-diene to p-nitrosotoluene, which should lead to formation of 2-p-tolyl-3,6-dihydro-orthoxazine (I), are presented in this paper:

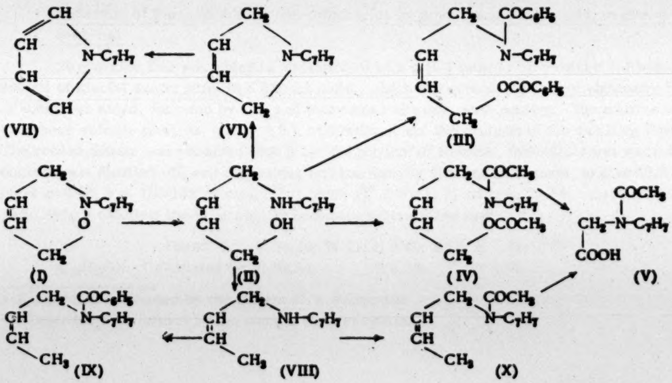

(I)

In our first experiment we left a sealed tube containing p-nitrosotoluene and excess of buta-1,3-butadiene in a cold water bath for a day, during which time the color of the solution changed from green to light brown. The tube was then opened, excess of butadiene was evaporated off, and the residue was recrystallized from cyclohexane and then from ethanol, to give colorless needles of the 1:1 addition product, $C_{11}H_{13}ON$, m.p. 46-47°, yield 57% of theory.

The next experiment was conducted at 0°, using organic solvents (chloroform, ether). The flask was removed from the ice bath after 1-2 days, the solvent was evaporated off, and the residue was steam- or vacuum-distilled, giving a yield of 80-90% of addition product.

The addition product was readily soluble in hot cyclohexane, methanol, ethanol, and ether, and in cold glacial acetic acid and chloroform, but is not soluble in water. It can be distilled without decomposition at reduced pressure (b.p. 112-113°/3mm) or with steam. It is shown to be 2-p-tolyl-3,6-dihydro-orthoxazine (I).

Reduction of the addition product with zinc dust in acetic acid gives 4-p-tolylaminobut-2-en-1-ol (II), which gives a crystalline dibenzoyl derivative (III), m.p. 130-131°, and a diacetyl derivative (IV) by the action of acetic anhydride, oxidation of which with potassium permanganate in acetone gives N-acetyl-N-tolylglycine (V).



Reduction of 2-p-tolyl-3,6-dihydro-orthoxazine (I) with zinc dust and acetic acid under more severe conditions gave 1-p-tolyl-2,5-dihydropyrrole (VI), also obtained by heating 4-p-tolylaminobut-2-en-1-ol with zinc chloride in acetic acid. Oxidation of 1-p-tolyl-2,5-dihydropyrrole (VI) with potassium permanganate or ferric chloride gives 1-p-tolylpyrrole (VII).

Reduction of 2-p-tolyl-3,6-dihydro-orthoxazine (I) with sodium and ethanol or n-butanol gave N-crotyl-p-toluidine (VIII), identified through its benzoyl derivative (IX) and acetyl derivative (X), oxidation of which with potassium permanganate in acetone gave N-acetyl-N-p-tolylglycine (V).

EXPERIMENTAL

Preparation of 2-p-tolyl-3,6-dihydro-orthoxazine

Experiment 1 *. 12.1 g (0.1 moles) of p-nitrosotoluene and 21 g of butadiene were placed in a tube cooled in an ethanol-solid carbon dioxide mixture, the tube was sealed, and was immersed in cold water (5-10°) for a day, shaking from time to time during the first 3 hrs. All of the p-nitrosotoluene passed into solution during the first 3.5 hrs. The solution was of a light brown color on the following day, and there were brownish-yellow crystals on the walls of the tube. The tube was cooled and opened, and excess butadiene was allowed to evaporate off. The residue was treated with hot cyclohexane (30 ml), and the solution was filtered hot, leaving a residue of about 0.8 g of a microcrystalline substance. Light yellow crystals separated from the filtrate, and were washed with cyclohexane and then twice recrystallized from 20 ml portions of ethanol, giving 10.0 g of colorless needles, m.p. 46-47°, yield 57% of theory.

Found %: C 75.51; 75.58; H 7.47; 7.44; N 8.18; 8.20
$C_{11}H_{13}ON$. Calculated %: C 75.40; H 7.48; N 7.99

Experiment 2 **. A flask containing 9.6 g (0.08 moles) of p-nitrosotoluene in 75 ml of chloroform was cooled in ice, and 11 g of butadiene was added. The flask was taken out of ice on the next day, and the solvent was distilled off. The residue was steam-distilled, and the crystalline product was recrystallized from methanol, to give 11.3 g of 2-p-tolyl-3,6-dihydro-orthoxazine, m.p. 46-47°, yield 81% of theory.

Experiment 3. 75 g of butadiene was added to a solution of 72.7 g (0.6 moles) of p-nitrosotoluene in 600 ml of chloroform, at 0°, and the solvent was distilled off after 24 hrs at 0°. The residue was vacuum-distilled, to give 94.2 g of 2-p-tolyl-3,6-dihydro-orthoxazine, b.p. 112-113°/3 mm, yield 90%. The product gave colorless needles, m.p. 47-48°, after a single recrystallization from ethanol.

Found %: C 75.40; 75.27; H 7.62; 7.83; N 7.97; 8.02
$C_{11}H_{13}ON$. Calculated %: C 75.40; H 7.48; N 7.99

Experiment 4. A solution of 30.3 g (0.25 moles) of p-nitrosotoluene and 35 g of butadiene in 500 ml of ether was kept at 0° for 2 days, the ether was distilled off, and the residue steam-distilled. The product separating from the distillate was recrystallized from methanol, giving 35.0 g of colorless needles of 2-p-tolyl-3,6-dihydro-orthoxazine, m.p. 47-48°, yield 80%.

Reduction of 2-p-tolyl-3,6-dihydro-orthoxazine by zinc dust in acetic acid, to give 4-p-tolylaminobut-2-en-1-ol

20 g of zinc dust was added to a solution of 17.5 g (0.1 mole) of 2-p-tolyl-3,6-dihydro-orthoxazine in 200 ml of glacial acetic acid, in a 500 ml bottle, which was corked and shaken vigorously for 10 min. 200 ml of water was added, followed by 275 g of potassium hydroxide, with cooling. The mixture was steam distilled, to remove volatile products, giving 0.5 l. of distillate, and the contents of the distilling flask were filtered hot. The cooled filtrate was extracted with 5 100 ml portions of benzene, the extract was washed with water, the benzene was distilled off, and the residue was fractionally distilled in vacuum, to give 13.8 g of 4-p-tolylaminobut-2-en-1-ol, b.p. 158-159°/3 mm, d_4^{20} 1.0553; n_D^{20} 1.5761; found MR_D 55.57; calculated MR_D 54.06; EMR_D 1.51, yield 78%; a colorless liquid, gradually becoming yellow when kept.

Found %: C 74.40; 74.21; H 8.80; 8.86; N 7.74; 7.72
$C_{11}H_{15}ON$. Calculated %: C 74.54; H 8.53; N 7.90

---

* Experiment performed by the student N. L. Fedyukina.

** Experiment performed by the student N. L. Fedyukina.

Dibenzoyl derivative of 4-p-tolylaminobut-2-en-1-ol

5.32 g (0.03 moles) of 4-p-tolylaminobut-2-en-1-ol in 10% sodium hydroxide solution (60 g) is shaken vigorously in a 100 ml bottle with 14.1 g of benzoyl chloride, added in 6 portions during 25 min. Excess of benzoyl chloride is then removed by heating the mixture. The crystalline product is dissolved in ether, and the solution is washed successively with water, 5% caustic soda, 3% hydrochloric acid, and again water. The ether is then distilled off, and the residue is dried in a desiccator over sulfuric acid, giving 11.0 g of ON-dibenzoyl derivative of 4-p-tolylaminobut-2-en-1-ol, m.p. 127.5-130°, yield 95%. The m.p. after two recrystallizations from ethanol is 130-131°.

Found %: C 77.88; 77.88; H 6.02; 6.24; N 3.74; 3.79

$C_{25}H_{23}O_3N$. Calculated %: C 77.90; H 6.02; N 3.63

Diacetyl derivative of 4-p-tolylaminobut-2-en-1-ol

A solution of 17.7 g (0.1 moles) of 4-p-tolylaminobut-2-en-1-ol in 60 ml of acetic anhydride was heated under reflux on a boiling water bath for 3.5 hrs., after which acetic acid and anhydride were distilled off in vacuum (50 mm), and the residue at 2 mm, to give 23.4 g of the diacetyl derivative of 4-p-tolylaminobut-2-en-1-ol, a colorless viscid liquid, b.p. 167-168°/2 mm, d_4^{20} 1.0855; n_D^{20} 1.5260; found MR_D 73.89; calculated MR_D 72.66; EMR_D 1.23. Yield 90%.

Found %: C 68.78; 68.67; H 7.40; 7.55; N 5.28; 5.25

$C_{15}H_{19}O_3N$. Calculated %: C 68.94; H 7.33; N5.36

Oxidation of the diacetyl derivative of 4-p-tolylaminobut-2-en-1-ol to N-acetyl-N-p-tolylglycine

A solution of 4.7 g (0.03 moles) of potassium permanganate in 300 ml of dry acetone was added during 165 min. with continual stirring to a solution of 2.61 g (0.01 moles) of the diacetyl derivative of 4-p-tolylaminobut-2-en-1-ol in 100 ml of dry acetone. The precipitate was collected on the following day, washed with acetone, and extracted with 50 ml of water. The aqueous extract was extracted with chloroform and was then made acid with dilute hydrochloric acid. The precipitate was collected, washed with cold water, and dried in a desiccator over sulfuric acid, to give 1.15 g (56% yield) of N-acetyl-N-p-tolylglycine, m.p. 173-176°, rising to 175.5-177° after recrystallization from hot water. Published m.p. data are 174-175° [3] and 175-176° [4].

Found %: C 63.79; 63.69; H 6.31; 6.34; N 6.79; 6.92

$C_{11}H_{13}O_3N$. Calculated %: C 63.75; H 6.33; N 6.76

The mixed m.p. with a specimen of N-acetyl-N-p-tolylglycine, m.p. 175-177°, prepared by oxidizing N-allylacet-p-toluidide with potassium permanganate in acetone, was 175-177°.

Conversion of 2-p-tolyl-3,6-dihydro-orthoxazine into 1-p-tolyl-2,5-dihydropyrrole

25 g of zinc dust was added to a solution of 17.5 g (0.1 moles) of 2-p-tolyl-3,6-dihydro-orthoxazine in 50 ml of glacial acetic acid, in a round-bottomed 250 ml flask fitted with a reflux condenser. The flask was shaken, when its contents became very hot, leading to vigorous boiling lasting for some minutes. The mixture was then boiled for 5 hrs, 100 ml of water was added to the cooled mixture, which was made alkaline with 40% caustic soda, and was steam distilled. Nearly colorless crystals separated from the distillate, and were collected and dried over sulfuric acid; 10.9 g (69% yield) of 1-p-tolyl-2,5-dihydropyrrole, m.p. 87-90°, were thus obtained. The m.p. rose to 92-93° after two recrystallizations from methanol.

Found %: C 83.06; 83.14; H 8.24; 8.24; N 8.68; 8.56

$C_{11}H_{13}N$. Calculated %: C 82.97; H 8.23; N 8.80

Conversion of 4-p-tolylaminobut-2-en-1-ol into 1-p-tolyl-2,5-dihydropyrrole

A mixture of 17.7 g (0.1 moles) of 4-p-tolylaminobut-2-en-1-ol, 10 g of anhydrous zinc chloride, and 50 ml of glacial acetic acid was boiled under reflux for 5 hrs., 100 ml of water and 100 g of sodium hydroxide were added to the cooled solution, and 1-p-tolyl-2,5-dihydropyrrole was distilled over with steam, and dried over sulfuric acid; yield 11.4 g (71%), m.p. 87-90°, raised to 92-93° by twice recrystallizing from methanol.

Oxidation of 1-p-tolyl-2,5-dihydropyrrole with potassium permanganate, to give 1-p-tolylpyrrole

A solution of 4.7 g (0.03 moles) of potassium permanganate in 300 ml of dry acetone was added, with constant stirring, during $2\frac{1}{4}$ hrs to a solution of 4.78 g (0.03 moles) of 1-p-tolyl-2,5-dihydropyrrole in 100 ml of dry acetone. The solution was filtered on the following day, and the acetone was distilled off from the filtrate. 50 ml of dilute (1:1) hydrochloric acid was added to the residue, which was then steam-distilled. The 1-p-tolylpyrrole collecting in the distillate was collected, washed with water, and dried over sulfuric acid; yield 2.20 g (47%), m.p. 81-83°, raised by recrystallization from methanol to 82-83°.

The product gave no depression of the m.p. of 1-p-tolylpyrrole, m.p. 82-83°, prepared from N-mucyl-p-toluidine. Published m.p. data are 82° [5] and 79-79.5° [6].

Oxidation of 1-p-tolyl-2,5-dihydropyrrole with ferric chloride, to give 1-p-tolylpyrrole

13.5 g (0.02 moles) of ferric chloride hexahydrate in 50 ml of water was added with stirring to a solution of 3.18 g (0.02 moles) of 1-p-tolyl-2,5-dihydropyrrole in 60 ml of 1:1 hydrochloric acid, and the mixture was steam distilled after an hour, to give 2.62 g (83% yield) of 1-p-tolylpyrrole, m.p. 82-83°, unchanged by recrystallization from ethanol. It did not depress the m.p. of a known specimen of 1-p-tolylpyrrole.

Reduction of 2-p-tolyl-3,6-dihydro-orthoxazine with sodium in ethanol, to give N-crotyl-p-toluidine

Experiment 1. 50 g (about 2.2 g-atoms) of sodium was added in large lumps during 10 min. to a boiling solution of 35.0 g (0.2 moles) of 2-p-tolyl-3,6-dihydro-orthoxazine in 650 ml of absolute ethanol in a round-bottomed 3 l. flask fitted with a reflux condenser, and the mixture was heated until all the sodium dissolved. It was then cooled and made acid with 1:1 hydrochloric acid, and steam distilled. It was then made alkaline with 40% caustic soda, and again steam distilled, collecting the light yellow oil which separated from the distillate, and extracting the aqueous layer of the distillate with 3 successive 100 ml portions of ether. The ether extract was added to the oil, and the solution was dried with anhydrous sodium sulfate. The ether was distilled off, and the residue was fractionally distilled in vacuum, giving 22.3 g of N-crotyl-p-toluidine, b.p. 96-97°/3 mm, d_4^{20} 0.9458; n_D^{20} 1.5505; found MR_D 54.34; calculated MR_D 52.53; EMR_D 1.81. Yield 69%. N-Crotyl-p-toluidine is a colorless, fairly mobile liquid, gradually becoming yellow; according to the literature its b.p. is 135°/33 mm [7].

Found %: C 81.85; 81.76; H 9.38; 9.27; N 8.55; 8.55
$C_{11}H_{15}N$. Calculated %: C 81.93; H 9.38; N 8.69

Experiment 2. 50 g (about 2.2 g-atoms) of sodium was added in large pieces during 10 min. to a boiling solution of 35.0 g (0.2 moles) of 2-p-tolyl-3,6- dihydro-orthoxazine in 700 ml of absolute n-butanol, in a 3 l. round-bottomed flask fitted with a reflux condenser with a broad inner tube. The mixture was then heated until all the sodium had dissolved; further manipulations were as in Experiment 1. 20 g of N-crotyl-p-toluidine was thus obtained, b.p. 96-97°/3 mm, d_4^{20} 0.9465; n_D^{20} 1.5505; found MR_D 54.30; calculated MR_D 52.53; EMR_D 1.77. Yield 62%.

Benzoylation of N-crotyl-p-toluidine

8.4 g (0.06 moles) of benzoyl chloride was added in 5 portions to 6.45 g (0.04 moles) of N-crotyl-p-toluidine in 40 g of 10% aqueous sodium hydroxide, during 20 min., shaking vigorously after each additional excess of benzoyl chloride was decomposed by heating. The benzoylation product was dissolved in ether, and the solution was washed successively with water, 5% aqueous sodium hydroxide, 5% hydrochloric acid, and again with water. The residue after distillation of ether was fractionally distilled in vacuum, giving 9.17 g of N-crotyl-benz-p-toluidide (IX), b.p. 168-170°/2 mm; d_4^{20} 1.0597; n_D^{20} 1.5781; found MR_D 83.09; calculated MR_D 81.26; EMR_D 1.83, yield 86%, a viscous, practically colorless liquid.

Found %: C 81.87; 81.90; H 7 29; 7.22; N 5.31; 5.20
$C_{18}H_{19}ON$. Calculated %: C 81.47; H 7.22; N 5.28

Acetylation of N-crotyl-p-toluidine

8.06 g (0.05 moles) of N-crotyl-p-toluidine and 15 ml of acetic anhydride were heated at 100° for 3 hrs under reflux. The acetic acid and anhydride were distilled off at 45 mm, and the residue was fractionally distilled at 3 mm, giving 9.20 g of N-crotyl-acet-p-toluidide (X), a colorless, viscous liquid, b.p. 120-120.5°/3 mm, d_4^{20} 1.0001; n_D^{20} 1.5292; found MR_D 62.71; calculated MR_D 61.77; EMR_D 0.94. Yield 91%.

Found %: C 77.08; 77.08; H 8.46; 8.47; N 7.16; 7.20
$C_{13}H_{17}ON$. Calculated %: C 76.81; H 8.43; N 6.89

Oxidation of N-crotyl-acet-p-toluidide to N-acetyl-p-tolylglycine

A solution of 4.7 g (0.03 moles) of potassium permanganate in 300 ml of dry acetone was added during 3 hrs. with constant stirring to 2.03 g (0.01 moles) of N-crotyl-acet-p-toluidide in 100 ml of dry acetone. The solution was filtered the next day, and the precipitate was washed with acetone and extracted with 50 ml of water. The aqueous extract was extracted with chloroform, made acid with dilute hydrochloric acid, and filtered. The precipitate was washed with cold water and dried in a desiccator over sulfuric acid; yield 0.56 g (27%) of N-acetyl-N-p-tolylglycine, m.p. 172-175°, rising to 175-177° after recrystallization from hot water, giving no depression with N-acetyl-N-p-tolylglycine, m.p. 175.5-177°, obtained by oxidation of the diacetyl derivative of 4-p-tolylaminobut-2-en-1-ol.

SUMMARY

1. The reaction between p-nitrosotoluene and buta-1,3-diene has been studied.

2. It has been shown that buta-1,3-diene adds on to p-nitrosotoluene according to the diene synthesis, to yield 2-p-tolyl-3,6-dihydro-orthoxazine.

Received January 2, 1952

Institute of Organic Chemistry
Academy of Sciences USSR
M. V. Lomonosov Moscow State University

LITERATURE CITED

[1] Yu. A. Arbuzov. Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 2, 344 (1952). *

[2] Yu. A. Arbuzov. Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 3, 547 (1952). **

[3] C. Paal, G. Otten, Ber. 23, 2587 (1890).

[4] C. A. Bischoff, A. Hausdorfer, Ber. 25, 2280 (1892).

[5] A. Pictet, Ber. 37, 2792 (1904).

[6] Yu. K. Yuriev. Ber. 59, 1944 (1936); J. Gen. Chem. 7, 267 (1937).

[7] W. J. Hickinbottom, J. Chem. Soc. 198 (1934).

---

* See Consultants Bureau English translation, p. 339.

** See Consultants Bureau English translation, p. 523.

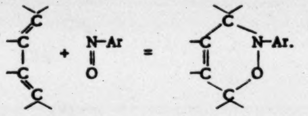
BLANK
PAGE

REACTIONS OF DIENE HYDROCARBONS WITH NITROSO-COMPOUNDS

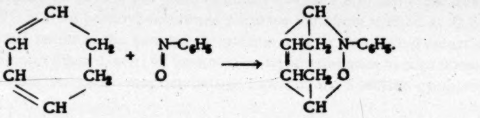
ADDITION OF CYCLOHEXA-1,3-DIENE TO NITROSOBENZENE

Yu. A. Arbuzov and T. A. Mastryukova

It has been shown in earlier communications [1,2] that buta-1,3-diene and other dienes (penta-1,3-diene, hexa-2,4-diene) condense with aromatic nitroso-compounds according to the diene synthesis, to give 3,6-dihydro-orthoxazine derivatives:



We shall in the present paper describe the results of a study of the reaction between cyclohexa-1,3-diene and nitrosobenzene, which should lead to the production of 2-phenyl-3,6-endoethyleno-3,6-dihydro-orthoxazine (I):



(I)

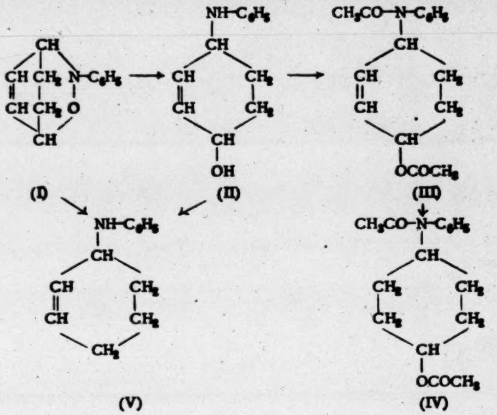
Cyclohexa-1,3-diene was prepared by the method of Ziegler [3], depending on bromination of cyclohexene with N-bromosuccinimide. We found that this was obtained in 67% yield only, applying Ziegler's method for bromination of succinimide, and his method was modified to give a 88% yield of N-bromosuccinimide. Bromination of cyclohexene with this gave 3-bromocyclohexene in 73% yield; elimination of hydrogen bromide by means of quinoline gave cyclohexa-1,3-diene in only 44% yield. Better results were obtained by the action of sodium acetate, which gave cyclohex-1-en-3-ol acetate in 89% yield, and this when heated with potassium bisulfate gave cyclohexa-1,3-diene in 66% yield.

Condensation of cyclohexadiene with nitrosobenzene proceeded smoothly in ether or ethanol at 0°, to give a colorless crystalline product, m.p. 65-66°, which was shown to be 2-phenyl-3,6-endoethyleno-3,6-dihydro-orthoxazine (I).

Reduction of the addition product with zinc dust in acetic acid gave a crystalline product, m.p. 64.5-65°, found to be 4-anilinocyclohex-2-en-1-ol (II), acetylation of which with acetic anhydride afforded the diacetyl derivative (III), m.p. 56-57.5°. The presence of a double bond in compound (III) was shown by its catalytic hydrogenation, which gave the diacetyl derivative of 4-anilinocyclohexan-1-ol (IV), m.p. 122-123°. (See top of next page).

It had previously been found [4] that reduction of 2-phenyl-3,6-dihydro-orthoxazine (produced by condensation of buta-1,3-diene with nitrosobenzene) with sodium in ethanol affords 1-anilinobut-2-ene, also obtained similarly from 4-anilinobut-2-en-1-ol (prepared by reduction of 2-phenyl-3,6-dihydro-orthoxazine with zinc dust and acetic acid).

Reduction with sodium in ethanol of 2-phenyl-3,6-endoethyleno-3,6-dihydro-orthoxazine (I) or of 4-anilinocyclohex-2-en-1-ol (II) should afford 3-anilinocyclohex-1-ene (V). This compound has not previously been described, and we synthesized it from 3-bromocyclohex-1-ene and aniline; its benzoyl derivative melted at 85-86°.



The expected amine (V) could not be isolated from the products of reduction of 2-phenyl-3,6-endoethyleno-3,6-dihydro-orthoxazine (I) with sodium in ethanol, which are a tarry mass. Reduction of 4-anilino-cyclohex-2-en-1-ol (II) with sodium in isoamyl alcohol gave a low yield of amine having a b.p. and refractive index close to those of 3-anilinocyclohex-1-ene (V), but the benzoyl derivative prepared therefrom melted at 72.5-74.5°. The reason for the difference in the melting points of the benzoyl derivatives may be that during reduction in isoamyl alcohol the double bond of the 3-anilinocyclohex-1-ene (V) formed may have undergone displacement. Noeldchen [5] observed this sort of isomerization during the reaction between sodium and 3-anilino-cyclopent-1-ene in isoamyl alcohol.

EXPERIMENTAL

Preparation of cyclohexa-1,3-diene

N-Bromosuccinimide. 17 ml of bromine was added during 80 min. to a solution of 32.0 g (0.323 moles) of succinimide and 12.8 g (0.32 moles) of sodium hydroxide in 70 ml of water, in a round-bottomed flask fitted with a stirrer and a dropping funnel, cooled in an ice-salt freezing mixture. The N-bromosuccinimide separating was collected, washed with 80 ml of ice water, and dried in a desiccator over calcium chloride, giving 50.8 g (88% yield) of N-bromosuccinimide.

3-Bromocyclohex-1-ene. A mixture of 150 ml of carbon tetrachloride, 82.1 g (1 mole) of cyclohexene, and 42.6 g (0.24 g-atoms of active bromine) was heated on a water bath for 90 min., in a round-bottomed flask fitted with a reflux condenser. The cooled solution was filtered, to remove succinimide, which was washed with 50 ml of carbon tetrachloride. The filtrate + washings were distilled, to remove carbon tetrachloride and unreacted cyclohexene, and the residue was fractionally distilled in vacuum to give 28.1 g (yield 73%) of 3-bromocyclohex-1-ene, b.p. 78-79°/39 mm.

Cyclohexa-1,3-diene. A mixture of 18.5 g (0.12 moles) of 3-bromocyclohex-1-ene and 46.5 g (0.36 moles) of freshly distilled quinoline in a 100 ml distilling flask fitted with a short fractionating column was heated in a metal bath at 140-150°, rising towards the end of the distillation to 170°; the receiver was immersed in freezing mixture. The distillate was washed with dilute hydrochloric acid and with water, and was dried over calcium chloride in presence of quinol, and then distilled from sodium, giving 4.08 g of twice-distilled cyclohexa-1,3-diene, b.p. 79.5-80°/736 mm; d_4^{20} 0.8394; n_D^{20} 1.4750; found MR_D 26.87; calculated MR_D 26.77. Yield 44%.

3-Acetoxycyclohex-1-ene. A mixture of 29.5 g (0.36 moles) of freshly fused sodium acetate, 120 ml of glacial acetic acid, and 40 g (0.25 moles) of 3-bromocyclohex-1-ene was left for 36 hrs, after which it was diluted with 350 ml of water, and made neutral with soda. The upper layer separating was washed with water, dried with fused caustic potash, and fractionally distilled in vacuum, to give 31.0 g (89% yield) of 3-acetoxycyclohex-1-ene, b.p. 58-69°/9 mm; d_4^{20} 1.0020; n_D^{20} 1.4588; found MR_D 38.24; calculated MR_D 38.13.

Cyclohexa-1,3-diene. A 50 ml distilling flask fitted with a short fractionating column and containing 30.2 g (0.215 moles) of 3-acetoxy-cyclohex-1-ene and 3 g of freshly fused potassium bisulfate was heated at 145-155°, cooling the receiver in a freezing mixture. The distillate was redistilled from 2 g of potassium bisulfate, and the distillate was washed successively with water, 5% caustic soda, and water, dried over calcium chloride in the presence of quinol, and again redistilled, giving 11.3 g (66% yield) of cyclohexa-1,3-diene, b.p. 80-80.5°/739 mm; d_4^{20} 0.8409; n_D^{20} 1.4751; found MR_D 26.83; calculated MR_D 26.77.

Preparation of nitrosobenzene

65 g of zinc dust was added in small portions during 20 min. to a mixture of 25 g of ammonium chloride in 800 ml of water and 50 g (42 ml) of nitrobenzene in a round-bottomed 1500 ml flask fitted with a mechanical stirrer; the temperature rose to 65° by the end of the reaction. The zinc oxide formed was filtered off and washed with 150 ml of hot water. The filtrate + washings were placed in a freezing mixture, when crystals of β-phenylhydroxylamine separated, and 130 ml of concentrated sulfuric acid was added when the temperature of the system had fallen to −2°, the mixture was shaken, replaced in the freezing mixture, and crushed ice was added to the solution of β-phenylhydroxylamine sulfate so obtained. A solution of 30 g of sodium dichromate in 100 ml of water at 0° was added rapidly to this solution when its temperature had fallen to −5°, the container was shaken for a few minutes, and the nitrosobenzene formed was collected on the filter pump, washed with water, and steam-distilled, cooling the receiver in ice. The nitrosobenzene collecting in the receiver was separated on the filter, washed with water, and dried in a desiccator over calcium chloride, giving 23.7 g (55% yield) of nitrosobenzene, m.p. 65-66°, not requiring any further purification.

Condensation of cyclohexa-1,3-diene with nitrosobenzene

Experiment 1. A flask containing 5.35 g (0.05 moles) of nitrosobenzene, 5.00 g (0.06 moles) of cyclohexa-1,3-diene, and 50 ml of ether was placed in an ice bath. Glistening crystals of the addition product began to appear within 2 hrs, and the reaction was completed within 24 hrs. The ether was then distilled off, and the product was recrystallized from ethanol, giving 8.45 g (90% yield) of a colorless microcrystalline product, m.p. 65-66°. 2-Phenyl-3,6-endoethyleno-3,6-dihydro-orthoxazine is readily soluble in hot methanol, ethanol, acetone, and cyclohexane, but is practically insoluble in water.

Found %: C 76.90; 76.95; H 7.00; 7.03; N 7.36; 7.47
$C_{12}H_{13}ON$. Calculated %: C 76.97; H 7.00; N 7.48

Experiment 2. A mixture of 5.35 g (0.05 moles of nitrosobenzene in 80 ml of ethanol and 5.00 g of cyclohexa-1,3-diene was kept at 0° for 24 hrs, the ethanol was distilled off on the water bath, and the residue was recrystallized from methanol, giving 8.05 g (86% yield) of 2-phenyl-3,6-endoethyleno-3,6-dihydro-orthoxazine, m.p. 65-66°.

4-Anilinocyclohex-2-en-1-ol (II)

8 g of zinc dust was added in 4 portions during 25 min., shaking vigorously after each addition, to a solution of 3.7 g (0.02 moles) of 2-phenyl-3,6-endoethyleno-3,6-dihydro-orthoxazine in 40 ml of glacial acetic acid, in a 100 ml bottle. 20 ml of water was then added, the solution was filtered, and the precipitate was washed with 30 ml of hot benzene. The filtrate was made neutral with aqueous sodium hydroxide, and the hot solution was extracted with 3 portions of benzene, the benzene was distilled off, and the residue was fractionated in vacuum, giving 3.6 g (96% yield) of 4-anilinocyclohex-2-en-1-ol, b.p. 168-168.5°/3.5 mm, 172.5-173.5°/5 mm, which crystallized after long standing. The m.p. was 64.5-65.5° after recrystallization from 1:1 ether-cyclohexane mixture.

Found %: C 76.22; 76.42; H 8.00; 7.96; N 7.32; 7.26
$C_{12}H_{15}ON$. Calculated %: C 76.16; H 7.99; N 7.40

The picrate was prepared from ethereal solution, and was recrystallized from ethanol, m.p. 142.5-143.5°.

Found %: N 13.43; 13.59
$C_{18}H_{18}O_8N_4$ Calculated %: N 13.39

Diacetyl derivative of 4-anilicocyclohex-2-en-1-ol (III)

A solution of 8.5 g (0.045 moles) of 4-anilinocyclohex-2-en-1-ol in 40 ml of acetic anhydride was heated at 100° under reflux for 3 hrs, acetic acid and excess of acetic anhydride were distilled off at 50 mm, and the residue was distilled at 3.5 mm, giving 12.0 g (98% yield) of the diacetyl derivative of 4-anilinocyclohex-2-en-1-ol, b.p. 181-182°/3.5 mm, a colorless viscous liquid which crystallized after long standing, m.p. after recrystallization from cyclohexane 56-57.5°

Found %: C 70.41; 70.59; H 6.99; 6.95; N 5.00; 4.93
$C_{16}H_{19}O_3N$. Calculated %: C 70.30; H 7.01; N 5.12

Diacetyl derivative of 4-anilinocyclohexan-1-ol (IV)

8.2 g (0.03 mole) of the diacetyl derivative of 4-anilinocyclohex-2-en-1-ol in 90 ml of dry ether was hydrogenated in presence of 1 g of platinized charcoal (10% Pt) at room temperature and ordinary pressure, 672 ml of hydrogen (at N.T.P.) being absorbed during 50 min. The solution was filtered from the catalyst, and the ether was distilled off. The crystalline residue was recrystallized from ligroin, to give 7.2 g (87% yield) of the diacetyl derivative of 4-anilinocyclohexan-1-ol, m.p. 122-123°.

Found %: C 69.90; 69.92; H 7.69; 7.57; N 4.88; 4.88
$C_{16}H_{21}O_3N$. Calculated %: C 69.79; H 7.69; N 5.08

Reduction of 4-anilinocyclohex-2-en-1-ol (II) with sodium in isoamyl alcohol

10.5 g of sodium is added in a few portions to a boiling solution of 5.5 g (0.03 mole) of 4-anilinocyclohex-2-en-1-ol in 220 ml of anhydrous isoamyl alcohol, in a liter flask fitted with a reflux condenser, and boiling was continued until all the sodium had dissolved. The solution was cooled and made acid with hydrochloric acid, and isoamyl alcohol was removed by steam distillation, and the residual solution was made alkaline with potash, and extracted with benzene. The benzene was distilled off, and the residue was vacuum distilled, to give 0.68 g of a product of b.p. 146-147°/13 mm, n_D^{20} 1.5803 (benzoyl derivative, m.p. 72.5-74.5°, from ethanol).

3-Anilinocyclohex-1-ene (V)

A solution of 20.4 g (0.127 mole) of 3-bromocyclohex-1-ene in 45 ml of absolute ether was added in small portions to 36.8 g (0.39 mole) of freshly distilled aniline. A precipitate formed immediately, and the solution became hot enough to boil gently. Sufficient 10% caustic soda was added the next day to dissolve the precipitate, the ether layer was separated, the aqueous layer was extracted with ether, the combined ethereal solutions were dried with fused caustic potash, the ether was distilled off, and the residue was fractionally distilled in vacuum, giving 18.3 g (83% yield) of 3-anilinocyclohex-1-ene, b.p. 132.5-133°/7 mm; d_4^{20} 1.0222; n_D^{20} 1.5804; found MR_D 56.42; calculated: MR_D 54.95; EMR_D 1.47.

Found %: C 83.30; 83.32; H 8.83; 8.93; N 7.85; 7.76
$C_{12}H_{15}N$. Calculated %: C 83.18; H 8.73; N 8.09

Benzoyl derivative of 3-anilinocyclohex-1-ene

2.1 g (0.015 mole) of benzoyl chloride was added in 3 portions, with vigorous shaking after each addition, to 1.7 g (0.01 mole) of 3-anilinocyclohex-1-ene suspended in 7 ml of 10% caustic soda. The precipitate was washed with water, and was recrystallized from ethanol, giving 1.97 g (72% yield) of the benzoyl derivative of 3-anilinocyclohex-1-ene, m.p. 85-86°.

Found %: C 82.31; 82.42; H 6.84; 6.88; N 5.09; 5.00
$C_{19}H_{19}ON$. Calculated %: C 82.28; H 6.90; N 5.05

SUMMARY

1. The reaction between cyclohexa-1,3-diene and nitrosobenzene has been studied.

2. It was found that the reaction proceeds according to the diene synthesis, with formation of 2-phenyl-3,6-endoethyleno-3,6-dihydro-orthoxazine.

Received October 15, 1951

Institute of Organic Chemistry
Academy of Sciences USSR, and
M. V. Lomonosov Moscow State University

LITERATURE CITED

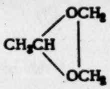
[1] Yu. A. Arbuzov, Proc.Acad.Sci.USSR,60,993(1948); Bull.Acad. Sci. USSR, Div.Chem.Sci.,No. 2, 344(1952).*
[2] Yu. A. Arbuzov and N. L. Fedyukina, Proc.Acad. Sci. U.S.S.R., 60, 1173 (1948).
[3] K. Ziegler, A. Spath, E. Schaaf, W. Schumann, E. Winkelmann, Ann.,551, 80 (1942).
[4] Yu.A. Arbuzov, Proc.Acad.Sci.USSR 63,531(1948); Bull. Acad. Sci. USSR, Div.Chem.Sci. No.3,547,(1952).
[5] F. Noeldehen, Ber,33, 3348 (1900).

* See Consultants Bureau Translation, p. 337. ** See Consultants Bureau Translation, p. 523.

SYNTHESES OF ACETALS OF ETHYLENE GLYCOL

M. F. Shostakovsky, N. A. Gershtein, and Z. S. Volkova

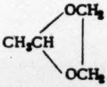
The acetals of ethylene glycol are undoubtedly of considerable theoretical and practical interest. Many derivatives of ethylene glycol, in particular its ethers are widely applied in various branches of industry and in laboratory practice [1-3]. The Russian scientists Markovnikov [4], Eltekov [5], and Favorsky [6] made important contributions to our knowledge of the properties of the α-glycols, including their general tendency towards isomerization into the appropriate aldehydes and ketones, including, in particular, the pinacolin rearrangement, and the mechanism of these transformations was elucidated [7]. These studies were also of practical significance, such valuable substances as Favorsky's dioxan, the importance of which can scarcely be overestimated, being obtained incidentally. Favorsky showed that a cyclic acetal (I) is formed at the same time as dioxan:



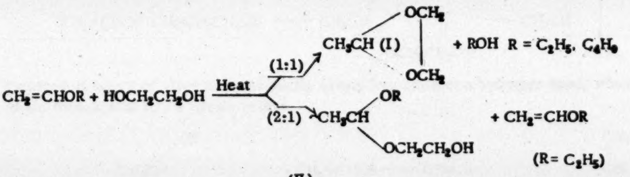
(I)

In spite of the symmetrical structure of the ethylene glycol molecule, it behaves in many reactions as a compound possessing two hydroxy groups of different reactivity, necessitating the provision of different conditions for preparation of its mono- and di-substituted derivatives, such as its mono- and di-ethers and -esters [8-13], or the mono- and di-alkylacetals.

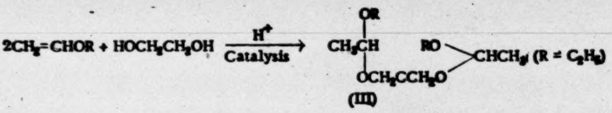
The latter group of substances is the subject of the present paper. The reason for the apparent nonequivalence of the hydroxy groups of ethylene glycol is that the reaction proceeds in stages. The symmetry of the molecule is abolished by formation of the mono-derivative, and the introduction of new radicals or groups also affects the reactivity of the remaining hydroxy group.

The alkylacetals of ethylene glycol were prepared by the method previously described by us, from monohydric alcohols and vinyl ethers [14-15]. The monoalkylacetals were prepared by the thermal method, and the dialkylacetals mostly by the catalytic method. The reaction leading to production of the cyclic acetal  proceeds very easily. Monoalkylacetals are obtained from vinyl ether and ethylene glycol when they are taken in the molar ratio 2:1, whereas when they are taken in equimolecular proportions the substance (I) is obtained instead of the expected monoalkylacetal. The dialkylacetals of ethylene glycol were obtained when ethylene glycol containing catalyst was added to the vinyl ether; adding the catalyst to the ether, or to the glycol-ether mixture, led to production of methyldioxan (I).

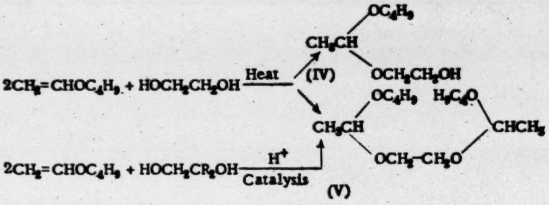
The reactions involved in the synthesis of alkylacetals of ethylene glycol may be represented by the following equations:



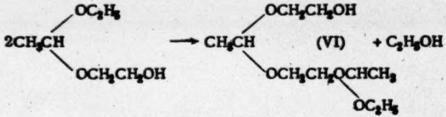
(II)



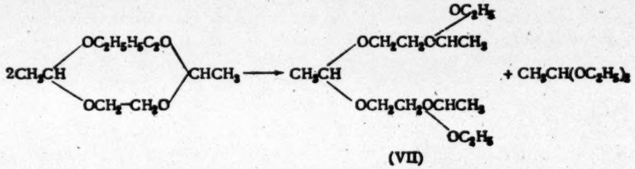
2CH₂=CHOR + HOCH₂CH₂OH
H⁺
Catalysis
OR
CH₃CH
OCH₂CCH₂O
RO
CHCH₃ (R = C₂H₅)
(III)



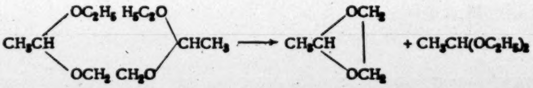
2CH₂=CHOC₄H₉ + HOCH₂CH₂OH
Heat
OC₄H₉
CH₃CH
(IV)
OCH₂CH₂OH
OC₄H₉ H₉C₄O
CH₃CH
CHCH₃
OCH₂-CH₂O
2CH₂=CHOC₄H₉ + HOCH₂CR₂OH
H⁺
Catalysis
(V)



OC₂H₅
2CH₃CH
OCH₂CH₂OH
OCH₂CH₂OH
CH₃CH
(VI)
+ C₂H₅OH
OCH₂CH₂OCHCH₃
OC₂H₅

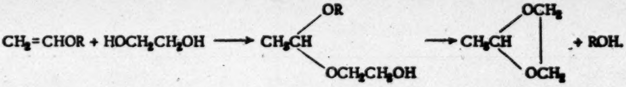


OC₂H₅H₅C₂O
2CH₃CH
CHCH₃
OCH₂-CH₂O
OC₂H₅
OCH₂CH₂OCHCH₃
CH₃CH
+ CH₃CH(OC₂H₅)₂
OCH₂CH₂OCHCH₃
OC₂H₅
(VII)



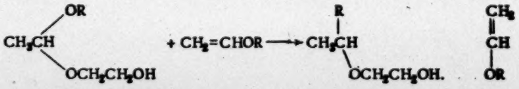
OC₂H₅ H₅C₂O
CH₃CH
CHCH₃
OCH₂ CH₂O
OCH₂
CH₃CH
OCH₂
+ CH₃CH(OC₂H₅)₂

It is very probable that acetalization of one of the hydroxy groups of ethylene glycol causes enhancement of the activity of the hydrogen atom of the remaining one, thus leading to cyclization of the monoacetal with elimination of alcohol:



CH₂=CHOR + HOCH₂CH₂OH
OR
CH₃CH
OCH₂CH₂OH
OCH₂
CH₃CH
OCH₂
+ ROH.

Presence of excess of vinyl ether evidently favors formation of a hydrogen bond, which hinders transformation of the monoacetal into a cyclic acetal:



OR
CH₃CH
OCH₂CH₂OH
+ CH₂=CHOR
R
CH₃CH
OCH₂CH₂OH.
CH₂
CH
OR

According to Shostakovsky's oxonium theory [17,18,19] presence of H ions in catalytic reactions activates the molecules of vinyl ethers, with formation of oxonium complexes, thanks to which the reaction proceeds more energetically, and involves both of the hydroxy groups of ethylene glycol.

EXPERIMENTAL

Synthesis of β-hydroxyethylethylacetal (II)

A mixture of 144 g (2 mole) of vinyl ethyl ether, b.p. 35.6-36°: 760 mm, (n_D^{20}; 1,3378; d_4^{20} 0.7531) and 62 g (1 mole) of ethylene glycol, b.p. 92.5°/8 mm; n_D^{20} 1.4320, was heated in a rotatory stainless steel autoclave, capacity 0.5 l., for 12-15 hrs. at 200-225°, pressures of 25-35 atm. being developed. The product was a homogeneous, mobile, straw-yellow liquid, weighing 194.6 g, losses due to vaporization of excess of vinyl ether amounting to 11.4 g.

The product was fractionally distilled in vacuum in a stream of nitrogen previously passed through alkaline pyrogallol solution, concentrated sulfuric acid, and alkali, successively. Two products were isolated, β-hydroxyethylethylacetal (II), b.p. 59.2-60°/2.5 mm (91.15 g, 68% yield), and the substance (VI), b.p. 129-130°/2 mm (7.75 g, 7% yield of ethylene glycol).

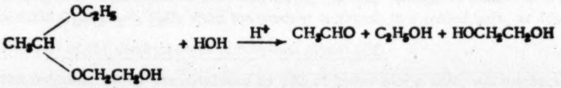
β-Hydroxyethylethylacetal has the following constants: b.p. 59.2-60°/2.5 mm, 55.75°/2 mm; n_D^{20} 1.4180; d_4^{20} 0.9753; MR_D 34.64; calculated for $C_6H_{14}O_3$ MR_D 34.719; found M 132.4; 132.6; calculated M 134.2.

Found %: C 53.80; 53.71; H 10.48; 10.54

$C_6H_{14}O_3$. Calculated %: C 53.73; H 10.45

β-Hydroxyethylethylacetal has not previously been described. It is a colorless, odorless, mobile, transparent liquid, soluble in ether, and benzene, readily soluble in ethanol and water, and reacting fairly energetically with sodium. Its structure was established by hydrolysis, with determination of the aldehyde, and by synthesis from it, as the alcoholic component, of acetal by the action of vinyl ethyl ether.

Hydrolysis of β-hydroxyethylethylacetal



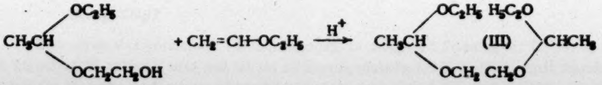
Hydrolysis with 2% sulfuric acid did not proceed to completion in the cold, the yields amounting to 88-94%. The method used by us was to heat the acetal in a sealed ampoule with 50 ml of 2% sulfuric acid for 2-4 hrs at 100°. The contents of the ampoule were then transferred to a volumetric flask, adding water to the mark, and taking 10 ml of the resulting solution for determination of acetaldehyde.

Acetaldehyde was determined by adding approximately 0.2 N sodium bisulfite, excess of which was titrated with 0.1 N iodine solution.* A sample of 0.5703 g of substance was hydrolyzed, and the volume of the product was made up to 200 ml. 4.25 ml of 0.1 N iodine was used to titrate 10 ml of the solution, corresponding with a value of 99.89% of the theoretical value. Results were calculated from the formula:

$$\% \text{ acetal} = \frac{(a-b)\cdot MK}{V\cdot 200},$$

where a is the number of ml of 0.1 N I_2 used in a blank titration, b is the number of ml of 0.1 N I_2 used in titration of excess of bisulfite, M is the mol. wt., K is the correction factor for the iodine solution (0.9662), and V is the weight of substance taken.

Acetalization of β-hydroxyethylethylacetal



---

* The method of determination is described in reference [16].

A drop of 33% hydrochloric acid was added as catalyst to a mixture of 34 g (0.25 mole) of β-hydroxyethylethylacetal and 18 g (0.25 mole) of vinyl ethyl ether. The reaction proceeded with liberation of heat, the temperature rising from 22° to 78°. The mixture was shaken from time to time, until the temperature ceased to rise, after which it was left overnight. The mixture was then fractionally distilled in a stream of nitrogen, giving 35.15 g (67.8% yield) of pure product (III), b.p. 85-85.5°/5 mm; 67.5-68° at 2 mm; n_D^{20} 1.4112; d_4^{20} 0.9274; MR_D 55.15; calculated for $C_{10}H_{22}O_4$ MR_D 54.952. Found M 189-190.8; calculated M 206.3.

Found %: C 57.80; 57.80; H 10.69; 10.85
$C_{10}H_{22}O_4$. Calculated %: C 58.25; H 10.68

Compound (III) is further described below, in the paragraph dealing with its synthesis from ethylene glycol. The preparation of the diacetal has been described in a Patent specification, which gave only the b.p. 97°/13 mm [20].

β-Hydroxyethyl-β-ethoxyethylideneoxyethylacetal (VI) is a colorless, odorless, transparent liquid, soluble in ether, and very soluble in ethanol and water, very hygroscopic, b.p. 129-130°; n_D^{20} 1.4408; d_4^{20} 1.063; MR_D 55.13; calculated for $C_{10}H_{22}O_5$ MR_D 55.163. Found mol. wt., determined cryoscopically in benzene solution, 224.8; 221, calculated for $C_{10}H_{22}O_5$, 222.3.

Found %: C 51.70; 51.92; H 9.95; 10.00
$C_{10}H_{22}O_5$. Calculated %: C 54.05; H 9.91

The difference between the actual and the theoretical analytical values is ascribable to the hygroscopicity of the product, and to possible formation of a hemihydrate, for which % C would be 51.95, and % H 9.96. This assumption is supported by the following facts: (a) repeated distillations always give a small amount of water, and (b) the product at first reacts very energetically with sodium, but the reaction soon slows down, usually taking 2-3 days for completion.

Analysis of the freshly distilled product gives a higher C content, although it is still less than the theoretical.

Found %: C 52.33; 52.40; H 9.84; 9.88
$C_{10}H_{22}O_5$. Calculated %: C 54.05; H 9.91

Hydrolysis is incomplete in the cold, being to only 90-91%, as compared with 98.92%, calculated from the composition $C_{10}H_{22}O_5 \cdot \frac{1}{2} H_2O$, when the product is heated in a sealed bulb, as described above.

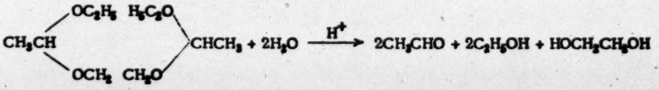
Synthesis of the diethylacetal of ethylene glycol (III)

The reaction, which was catalyzed by 33% of hydrochloric acid, was conducted in a flask fitted with a reflux condenser, a mechanical stirrer with a mercury seal, a thermometer, and a dropping funnel. Ethylene glycol containing 0.025-0.05 g of hydrochloric acid per 0.5 mole of compound (III) was added drop by drop to vinyl ethyl ether in the flask; an inverse order of addition of the components converted the reaction towards production of the cyclic acetal (I). The experimental conditions are given in the Table. Two products were obtained in all cases; the expected dialkylacetal (III) and a higher b.p. product (VII).

The acetal (III) had the following physical constants: b.p. 92°/9 mm; 86° at 6 mm; n_D^{20} 1.4110; d_4^{20} 0.9274; MR_D 55.14; calculated for $C_{10}H_{22}O_4$ MR_D 54.952, cryoscopically determined molecular weight (in benzene) 190.9, 203.8, calculated M 206.3.

Found %: C 57.91; 58.32; H 10.75; 10.78
$C_{10}H_{22}O_4$. Calculated %: C 58.25; H 10.68

Hydrolysis of the dialkyldiacetal of ethylene glycol (III)



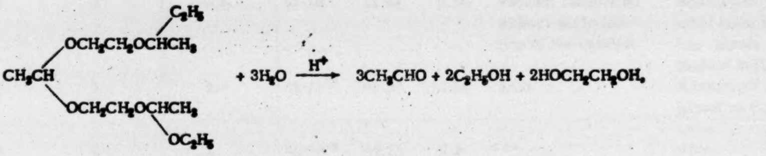
$$CH_3CH\begin{matrix}OC_2H_5 & H_5C_2O\\ OCH_2 & CH_2O\end{matrix}CHCH_3 + 2H_2O \xrightarrow{H^+} 2CH_3CHO + 2C_2H_5OH + HOCH_2CH_2OH$$

Hydrolysis was performed without heating, in stoppered Erlenmeyer flasks, in which the sample was shaken with 25 ml of 2% sulfuric acid and 25 ml of approximately 0.2 N $NaHSO_3$ until dissolution is complete, when it was left for 15 min., and excess of bisulfite was titrated with 0.1 N iodine. The content of diethylacetal of ethylene glycol (III) thus found was 98.59% and 99.57% of the theoretical value, calculated for (III). The diethyltriacetal of ethylene glycol (VII) had b.p. 149.5-150°/2 mm; n_D^{20} 1.4235; d_4^{20} 0.9747; MR_D 76.81; calculated for $C_{14}H_{30}O_6$ 76.710. Found M 277.3; 280.0; calculated M 294.

Found %: C 57.34; 57.11; 57.00; H 10.41; 10.32; 10.26

$C_{14}H_{30}O_6$. Calculated %: C 57.14; H 10.20

Hydrolysis of the diethyltriacetal of ethylene glycol, which proceeds according to the equation



shows that our product contains 97.86% or 97.65% of substance (VII).

The results agree with the formula proposed for the substance. In addition to the products enumerated, an additional fraction, boiling over the range of temperatures from 168° to over 200°, with partial decomposition, and of which the highest b.p. fractions partially solidified in the condenser, was obtained. The latter fraction, amounting to a yield of about 1.5%, was not further investigated.

Synthesis of β-hydroxyethylbutylacetal (IV)

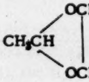
Experiment 1. β-Hydroxyethylbutylacetal was synthesized similarly to β-hydroxyethylethylacetal (II). The cyclic acetal (I) was obtained instead of the expected acetal when vinyl n-butyl ether and ethylene glycol were taken in equimolecular proportions. 53 g of vinyl n-butyl ether, b.p. 93.2-93.8°/76 mm; n_D^{20} 1.4026; d_4^{20} 0.7790 and 31 g of ethylene glycol, b.p. 96°/7 mm; n_D^{20} 1.4320, gave after the first fractionation: Fraction 1, obtained by cooling the condenser spiral to −14-15°, at 2 mm: 29.57 g; n_D^{20} 1.3982;

Fraction 2, b.p. up to 35°/2 mm; 36.17 g; n_D^{20} 1.4018.

Residue in the distilling flask, separating into two layers, 6.20 g.

Fraction 1, after treatment with sodium, gave 28 g of the cyclic acetal of ethylene glycol, b.p. 81.5-82.5°, n_D^{20} 1.3975; d_4^{20} 0.9823; found MR_D 21.64; calculated for $C_4H_8O_2$ MR_D 21.758.

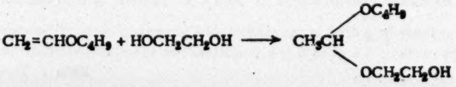
Fractional distillation of fraction 2 at atmospheric pressure gave 35.6 g of butanol, b.p. 116-118°; n_D^{20} 1.3995. The residue gave 2.7 g of dibutylacetal, b.p. 181-184°/758 mm; n_D^{20} 1.4080, and 1.7 g of butanol, b.p. 115-120°. The reaction thus gave:

1)  ... 28.0 g (68.6% of theory);

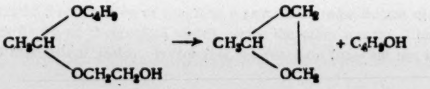
2) C_4H_9OH ... 37.3 g (95% of theory);

3) $CH_3CH(OC_4H_9)_2$ ... 2.7 g (5.86% of theory).

These data show that the reaction may be represented by the equations:



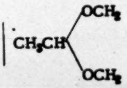
$$CH_2=CHOC_4H_9 + HOCH_2CH_2OH \longrightarrow CH_3CH\begin{matrix}OC_4H_9\\OCH_2CH_2OH\end{matrix} \qquad (I)$$

 (II)

$$CH_2=CHOC_4H_9 + C_4H_9OH \longrightarrow CH_3CH(OC_4H_9)_2. \qquad (III)$$

TABLE

Synthesis of the diacetal of ethylene glycol

Expt. No.	Ratio of reagents		Moles of HCl catalyst (30%)	% Yield of basic product	% Yield of by-product	Method of treatment of the reaction products and of isolation of the individual fractions	Remarks
	$CH_2{=}CH{-}O{-}C_2H_5$, mole	$HOCH_2{-}CH_2OH$ mole					
1	1	0.5	$42 \cdot 10^{-5}$	11.41	2.95	Vacuum distillation without neutralization of the catalyst	Addition of vinyl ethyl ether to ethylene glycol. Basic product is (I).
2	1	0.5	$42 \cdot 10^{-5}$	68.98	18.84	ditto	Addition of ethylene glycol to vinyl ethyl ether
3	2	1	$42 \cdot 10^{-5}$	61.22	7.3	"	ditto
4	2	1	$42 \cdot 10^{-5}$	66.6	20.1	Neutralization of catalyst with solid K_2CO_3, and vacuum distillation of filtrate	"
5	2	1	$42 \cdot 10^{-5}$	63.4	17.2	ditto	"
6	2	1	$42 \cdot 10^{-5}$	42.88	12.31	Neutralization with 2% K_2CO_3, washing with water, drying over K_2CO_3, and vacuum distillation	"
7	2	0.5	$42 \cdot 10^{-5}$	65.97	12.95	Treatment of the reaction products with sodium, followed by vacuum distillation	"
8	0.5	0.5	$42 \cdot 10^{-5}$	–	–	Vacuum distillation	Sole product is the cyclic acetal  $CH_3CH\langle^{OCH_2}_{OCH_2}$

NOTE. It appears from the Table that the best yields are obtained with a ratio of reagents of 2:1, adding ethylene glycol + catalyst to vinyl ethyl ether. The opposite order of addition, and also a ratio of 1:1, as in Expts. 1 and 8, lead to formation of cyclic acetal.

Experiment 2. Experimental conditions as above, but the ratio of vinyl n-butyl ether to ethylene glycol was 2:1 mol. 100 g of vinyl n-butyl ether and 31 g of ethylene glycol gave 127.6 g of liquid product (losses 3.4 g), the first fractionation of which gave:

Fraction 1, b.p. 26-30° at 8 mm, 31.17 g (condenser spiral cooled to −14°)
Fraction 2, b.p. 32-72° at 3 mm, 10.53 g.
Fraction 3, b.p. 73-85° at 3 mm, 5.73 g.
Fraction 4, b.p. 138-147° at 3 mm, 58.31 g.
Fraction 5, b.p. 163-234° at 3 mm, 13.00 g with decomposition.

Fraction 1, after treatment with sodium, gave 28.5 g of vinyl n-butyl ether, b.p. 93-93.6° at 758 mm n_D^{20} 1.4025. Similar treatment of Fractions 2 and 3 gave 9.8 g (about 6% of theoretical) of dibutylacetal, b.p. 183-186°; n_D^{20} 1.4088.

Triple fractionation of Fraction 4 gave two products, one of which was β-hydroxyethylbutylacetal (IV) (17.5 g, or 21.6% of theoretical yield), while the other was the dibutyldiacetal of ethylene glycol (V) (21.2 g, or 16% of theoretical yield). Prolonging the reaction time did not lead to production of higher yields of the products.

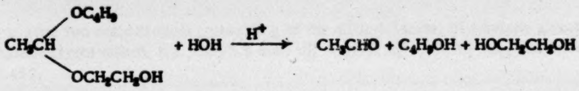
β-Hydroxyethylbutylacetal is a colorless, transparent liquid, b.p. 78-79° at 2 mm; 92-93° at 3 mm; n_D^{20} 1.4250; d_4^{20} 0.9435; MR_D 43.88; calculated for $C_8H_{18}O_3$ MR_D 43.955; found M 161.3; 161.4; calculated M 162.22.

Found %: C 59.40; 59.19; H 11.20; 10.93

$C_8H_{18}O_3$. Calculated %: C 59.26; H 11.11

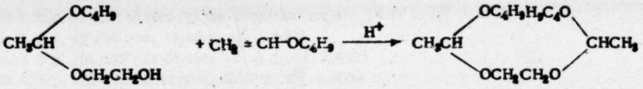
The structure of substance (IV) was established by its hydrolysis, and by the synthesis from it of substance (V), by reaction with vinyl n-butyl ether.

Hydrolysis of β-hydroxyethylbutylacetal proceeds in accordance with the equation



under the same conditions as for the preceding product, and indicate a content of β-hydroxyethylbutylacetal (IV) of 98.31% or 99.03%.

Acetalization of β-hydroxyethylbutylacetal



9.5 g of substance (IV) and 6.0 g of vinyl n-butyl ether in presence of catalyst gave 12.8 g of substance (V), a yield of 85.5%. It had b.p. 120.5-121° at 2 mm; n_D^{20} 1.4220; d_4^{20} 0.9072; MR_D 73.50; calculated for $C_{14}H_{30}O_4$ MR_D 73.424; found M 274.8; 274.2; calculated M 262.4.

Found %: C 64.65; 64.36; H 11.64; 11.58

$C_{14}H_{30}O_4$. Calculated %: C 64.13; H 11.45

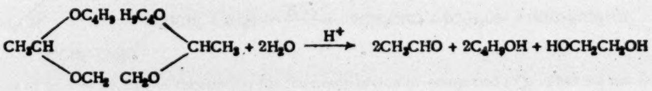
The structure of compound (V) has thus been established in two ways, and is beyond doubt.

Compound (V), obtained in the synthesis of compound (IV), has b.p. 120-121° at 2 mm; 128-129° at 2.5 mm; 137-138° at 3 mm; n_D^{20} 1.4220; d_4^{20} 0.9095; MR_D 73.20; calculated for $C_{14}H_{30}O_4$ MR_D 73.424; found M 254.7; 256.8; calculated M 262.4.

Found %: C 63.81; 63.94; H 11.60; 11.61

$C_{14}H_{30}O_4$. Calculated %: C 64.13; H 11.45

Hydrolysis of the dibutylacetal of ethylene glycol (V)



showed a content of compound (V) of 97.88% or 98.3%.

It was not possible to separate individual fractions of the higher b.p. fractions, as they undergo decomposition even at pressures of the order of hundredths of a mm.

Catalytic synthesis of the dibutyldiacetal of ethylene glycol (V)

Two experiments were performed, applying the same conditions as for synthesis of the diacetal (III). The reaction products of the first experiment, without preliminary neutralization of the catalyst, were fractionally distilled under reduced pressure in a stream of nitrogen. In the second experiment the catalyst was first neutralized with solid potassium carbonate.

Experiment 1. 93 g (1.5 mole) of ethylene glycol with 2 drops of 33% hydrochloric acid was added drop by drop to 300 g (3 mole) of vinyl n-butyl ether. The reaction products were fractionated under reduced pressure, in a stream of nitrogen. The first fractionation gave the following results:

Fraction 1, b.p. 20-21°/4 mm, 73.9 g; n_D^{20} 1.4008 (condensed in a spiral cooled at −14° to −15°).
Fraction 2, b.p. 21-66°/4 mm (bulk at 64-66°), 47.4 g, n_D^{20} 1.4055.
Fraction 3, b.p. 66°/4 mm, 154.6 g; n_D^{20} 1.4147.
Fraction 4, b.p. 125-135° at 3 mm (bulk at 133-135°); n_D^{20} 1.4227.
The residue of 20.5 g decomposes at its b.p.

Fraction 1, after treatment with sodium, gave 72.0 g of cyclic acetal of b.p. 81.5-82°; n_D^{20} 1.3987; d_4^{20} 0.9798; MR_D 21.67; calculated for $C_4H_8O_2$ MR_D 21.758.

Fractions 2 and 3 when similarly treated with sodium gave 176.3 g of dibutylacetal, b.p. 64°/2.5 mm; n_D^{20} 1.4090.

Fractions 4, after two redistillations , gave 65 g of the dibutyldiacetal of ethylene glycol (14% yield, calculated on ethylene glycol taken), b.p. 128°/2.5 mm; n_D^{20} 1.4222: d_4^{20} 0.9079; MR_D 73.33; calculated for $C_{14}H_{30}O_4$ MR_D 73.422.

Experiment 2. The experimental conditions were the same as before, taking 93 g of ethylene glycol (1.5 mole), and 300 g (3 mole) of vinyl n-butyl ether. After completion of the reaction the product was treated with anhydrous potassium carbonate, in order to neutralize the catalyst, filtered, and the filtrate was fractionally distilled as before. The results of the first fractionation were:

Fraction 1, b.p. 20-21°/40 mm (in the condenser spiral), 19.87 g; n_D^{18} 1.4070.
Fraction 2, b.p. 40°/40 mm, 11.80 g; n_D^{18} 1.4090.
Fraction 3, b.p. 101-105°/42-45 mm, 64.35 g; n_D^{18} 1.4125.
Fraction 4, b.p. 125-172° at 42 mm, 229.0 g; n_D^{18} 1.4235.
Residue 36.25 g; n_D^{18} 1.4145.

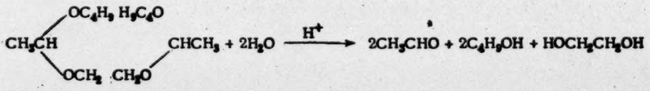
The first three fractions were shaken with 2% potassium carbonate solution, and then repeatedly with water, dried with anhydrous potassium carbonate, and redistilled, giving 25.6 g of dibutylacetal, b.p. 182-185°, n_D^{20} 1.4085.

Repeated redistillation of Fraction 4 gave 35 g of a substance with the physical constants of compound (V). The bulk of Fraction 4 was dibutylacetal.

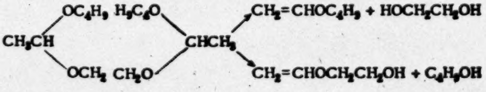
Product (V) from both experiments, after redistillation, boiled at 128-130°/2.5 mm; n_D^{20} 1.4220; d_4^{20} 0.9075; MR_D 73.36; calculated for $C_{14}H_{30}O_4$ MR_D 73.424; found M 251.8; 256.3; calculated M 262.3.

Found %: C 64.27; 64.11; H 11.62; 11.47
$C_{14}H_{30}O_4$. Calculated %: C 64.13; H 11.45

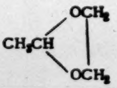
Hydrolysis of the dibutyldiacetal of ethylene glycol (V)



gave values of 98.6 or 99.82% of theoretical for the composition of compound (V). Thus we see that the reaction between vinyl butyl ether and ethylene glycol in presence of HCl catalyst leads to production of the dibutyldiacetal of ethylene glycol (V), although only in 15% yield. The results indicate that the diacetal (V) is very unstable, undergoing decomposition in two directions during distillation:



followed by cyclization, to give the acetal



and by formation of dibutylacetal by reaction between vinyl n-butyl ether and butanol. Evidently increase in the size of the radical R in ethylene glycol acetals with open chains renders them less stable.

SUMMARY

1. The conditions for synthesis of β-hydroxyethylalkylacetals have been worked out.

2. Conditions for synthesis of dialkylacetals have been elucidated.

3. Their tendency towards disproportionation with further transformations has been demonstrated.

4. Of the 6 compounds synthesized 5 have not previously been prepared or described.

5. A mechanism explaining the transformations is presented.

Received November 20, 1951

Institute of Organic Chemistry
Academy of Sciences USSR

LITERATURE CITED

[1] P. V. Zimakov, Ethylene Oxide, 1946, p. 194.

[2] ibid., p. 195.

[3] US.Pat. 2406504 (1946); 2382874 (1945); 2364438 (1944). Brit. Pat. 601612 (1948); US.Pat. 2442804 (1948) and others.

[4] V. V. Markovnikov, Thesis, Kazan, 1869.

[5] A. P. Eltekov, J. Russ. Phys. Chem. Soc., 14, 355 (1882).

[6] A. E. Favorsky, J. Russ. Phys. Chem. Soc., 38, 74 (1906).

[7] A. E. Favorsky, J. Russ. Phys. Chem. Soc., 38, 741 (1906).

[8] M. H. Palomaa, Ber. 35, 3300 (1902).

[9] A. Wurtz, Ann. Chim. (3), 55, 431 (1895).

[10] Walter Lippert, Ann. 276, 174 (1893).

[11] Yu. A. Drushell, G. R. Bancroft, C. 1918, p. 916.

[12] F. Telegen, Rec. Trav. chim. Pays-Bas 57, 667 (1938).

[13] M. B. Turova-Polyak, J. Appl. Chem., 9, 696 (1936).

[14] N. A. Gershtein and M. F. Shostakovsky, J. Gen. Chem., 18, 451 (1948).

[15] M. F. Shostakovsky and N. A. Gershtein, J. Gen. Chem., 16, 937 (1946).

[16] N. A. Gershtein and M. F. Shostakovsky, J. Gen. Chem., 18, 1989 (1948).

[17] M. F. Shostakovsky, J. Gen. Chem., 13, 674 (1943).

[18] M. F. Shostakovsky, J. Gen. Chem., 14, 102 (1944).

[19] M. F. Shostakovsky, J. Gen. Chem., 14, 1143 (1946).

[20] D. R. Patent, C. 1931, 27.

BLANK
PAGE

SYNTHESIS AND POLYMERIZATION OF VINYLCAPROLACTAM

M. F. Shostakovsky, N. A. Medzykhovskaya, and M. G. Zelenskaya

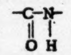
The development of polymerization processes as a basis for production of high molecular substances has led to the intensive development of methods of synthesis of unsaturated compounds, and to a study of their chemical properties [1]. Vinyl ethers have assumed considerable importance during the past decade, and their synthesis has been based on the reaction of vinylation, introduced by Favorsky and Shostakovsky [2]. Attention was directed basically in these studies towards the reaction between acetylene and alcohols, and towards the investigation of the properties and transformations of the ethers obtained [2].

Much less attention has been devoted to the study of the products of reaction of acetylene with compounds containing nitrogen or sulfur. Most of the published references to nitrogen-containing vinyl derivatives and their polymers are in the patent literature, although this class of compounds is of considerable interest [3]. A study of the conditions of preparation of these compounds, and of their properties and characteristic reactions may provide us with a much more profound understanding of the mechanism of transformation of various vinyl derivatives.

Of the group of nitrogen-containing vinyl compounds N-vinyl-pyrrolidone [4] is of particular interest, in view of its polymer. It is synthesized usually in the following way:

butane-1,4-diol → γ-butyrolactone → pyrrolidone → vinylpyrrolidone.

The polyvinylpyrrolidone molecule contains the carbamido-group, similarly to proteins:

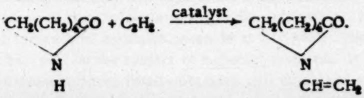


$$-\underset{\underset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-$$

Our studies included preliminary investigations of synthesis of pyrrolidone by the above reactions, as well as work on vinylcaprolactam and its polymer, since these are based on materials which are readily available, and which have been widely used in our industry.

It may be supposed that polyvinylcaprolactam, the molecule of which also contains the carbamido-group, should possess a number of valuable properties. There are no references in the literature to polyvinylcaprolactam, and only brief references to vinylcaprolactam in the American patent literature, whereby vinylation of caprolactam is conducted in toluene solution by means of acetylene diluted with nitrogen, in presence of potassium salt of pyrrolidone as a catalyst. The vinylation of pyrrolidone and its derivatives (methylpyrrolidone) and homologs (piperidone and ϵ-caprolactam) was conducted in the presence of known catalysts of this process (alkalis, alkoxides) and of less widely known catalysts, such as salts of lactams, imides, and amides. Solvents which may be used in the process are toluene, decalin, and vinyl ethers [5].

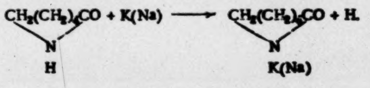
In the preparation of vinylcaprolactam we took potassium hydroxide as the catalyst, as well as the potassium salt of ϵ-caprolactam, which we were the first to apply for this purpose. The solvents used were vinyl butyl ether or toluene. Vinylation proceeds only very slowly, even at 170-175°, using powdered potassium hydroxide as the catalyst and vinyl butyl ether as the solvent; the reaction mixture contained a large amount of unreacted ϵ-caprolactam, with tarry products, but only traces of vinyl compound. Much better results were obtained with potassium salt of ϵ-caprolactam as catalyst, when the yields of vinyl derivative were 71% of theoretical.



$$\underset{\underset{H}{N}}{CH_2(CH_2)_4CO} + C_2H_2 \xrightarrow{\text{catalyst}} \underset{\underset{CH=CH_2}{N}}{CH_2(CH_2)_4CO.}$$

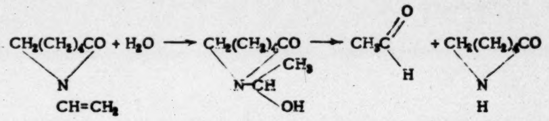
Vinylation was effected with undiluted acetylene, which was shown by Shostakovsky to give good results in the preparation of vinyl ethers. The vinylcaprolactam so obtained was a crystalline substance, which has not previously been reported. It is very hygroscopic, and when left in contact with the atmosphere it can absorb an equimolecular amount of water; the hydrate so obtained does not crystallize.

The product of reaction of potassium or sodium with such lactams as pyrrolidone is usually termed the potassium or sodium salt of the lactam, and we accordingly call our catalyst the potassium salt of ε-caprolactam:



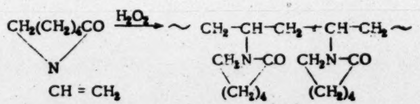
We found that the amount of hydrogen evolved when potassium is added to ε-caprolactam is considerably less than would follow from the above equation, suggesting that much of it is used in some hydrogenation reaction. It might be supposed that the resulting products could be 6-aminohexanol ($NH_2CH_2-(CH_2)_4CH_2OH$), as well as hexamethyleneimine $CH_2(CH_2)_4CH_2$ N H and other products. There are grounds for believing that these products are formed by the action of sodium on caprolactam in ethanol solution.

Hydrolysis of vinylcaprolactam with dilute sulfuric acid gives ε-caprolactam and acetaldehyde, through the semi-acetal:



ε-Caprolactam is obtained in small yields only from the reaction mixture, owing, in our opinion, to formation of water-soluble-aminocapronic acid and its salts; it is known that heating of ε-caprolactam with acids leads to formation of ε-aminocapronic acid $H_2NHC_2-(CH_2)_4COOH$ [6]. By subjecting ε-caprolactam to the action of acid, under the same conditions as for hydrolysis of vinylcaprolactam, we were able to recover only very small amounts of ε-caprolactam.

Vinylcaprolactam is not so readily hydrolyzable as are the vinyl ethers, suggesting that during vinylation ε-caprolactam reacts as a lactam, giving N-vinyl derivatives. It is known that with excess of reagent and at higher temperatures ε-caprolactam gives principally N-derivatives, and that O-derivatives when formed are transformed into N-derivatives when heated [8]. A fall in the yield of free aldehyde produced is observed when the temperature of hydrolysis is raised, due to the tendency of the aldehyde to condense with amino-acid, to give N-alkylidene derivatives. We did not in the present research make any more detailed study of the conditions of full hydrolysis of vinylcaprolactam. The process of polymerization of vinylcaprolactam is of considerable interest:



A preliminary test of the capacity for polymerization of vinylcaprolactam, taking as catalyst ferric chloride, which is widely applied to the polymerization of vinyl ethers [8] did not give the desired results; this is further evidence that our product is the N-vinyl, and not the O-vinyl derivative.

Formation of polymer was not observed with benzoyl peroxide at 55-60°; we found that activation of the vinylcaprolactam molecule by peroxides requires a temperature higher than 100°. The high temperature required for polymerization of vinyllactams (vinylcaprolactam, vinylpyrrolidone) appears to be due to the lowering of the reactivity of the ethylene bond by presence in the molecule of the carbamido-group. We were able to effect polymerization of vinylcaprolactam in presence of hydrogen peroxide at 140-150°. The elucidation of the structure of the links of the resulting chain will be the subject of a special research. It should be noted that under our conditions of polymerization the reaction mixture finally obtained still contained monomer, which could be distilled off from the polymer, and redistillation of this monomer gave rise to formation of considerable amounts of polymer. This effect may be ascribed to presence in the monomer of traces of a volatile crystalline product formed from hydrogen peroxide and caprolactam in presence of air, and this product is, as will be shown below, an initiator of the polymerization process.

Polyvinylcaprolactam is a faintly yellow powder, readily soluble in cold water, benzene, and ethanol, but insoluble in ether and gasoline. When the aqueous solution of the polymer is heated the polymer separates out, returning into solution when the water cools; this shows that desolvation takes place.

A study of polymerization of aqueous emulsions, in the presence or absence of certain basic neutralizing substances (ammonia, amines), is of considerable importance. We were able to isolate a hitherto unknown crystalline intermediate product of polymerization of vinylcaprolactam, which gave peroxide reactions, and which was formed when vinylcaprolactam was heated with hydrogen peroxide with access of air. Determination of the molecular weight of this product suggests that it consists of two molecules of vinylcaprolactam and one of oxygen $C_{16}H_{26}N_2O_4$ (M 310). We were able to show that the product acts as an initial active center for the growth of the polymer chain, and is thus an initiator of the process of polymerization of unsaturated compounds, in particular of vinylcaprolactam.

It may be supposed that the process proceeds in two directions in presence of air. In one, the vinylcaprolactam molecule enters into reaction, after activation by peroxide (or rather by atomic oxygen arising from decomposition of peroxide), with other, inactive vinylcaprolcatam molecules, to give polymer. In the other direction the active molecule reacts with atmospheric oxygen to give the above mentioned peroxide compound, which then breaks down and can initiate the polymerization process.

We have only the block polymerization of vinylcaprolactam over a narrow range of temperatures, and in presence of air. It would be of great interest to study this process in the absence of atmospheric oxygen, since this should lead to a considerable increase in its velocity, due to the exclusion of the possibility of formation of the intermediate peroxide product. Formation of polymer by thermopolymerization is insignificant at these temperatures (140-150°).

EXPERIMENTAL

Preparation of vinylcaprolactam

A solution of 198 g of ϵ-caprolactam in about 200 g of toluene is put into a stainless steel rotary 2000 ml autoclave containing catalyst, and fitted with a manometer, a thermometer, and a micro-valve for introduction of gas. The catalyst is prepared from 28 g of ϵ-caprolactam in 150 ml of toluene and 9.7 g of potassium at 60-80°. The total charge of the autoclave, in g., is

ϵ-caprolactam	226
Toluene	400
Potassium	9.7

The amount of caprolactam taken for preparation of the catalyst amounts to 12-12.5% of the total taken for the reaction. The autoclave is filled with acetylene, and heated; absorption of acetylene proceeds energetically at about 100°, and heating is then stopped (maximum temperature 125°). The autoclave is allowed to cool, when a further charge of acetylene is given, and the temperature is again raised to 100-125°. These operations are repeated until there is no further absorption of acetylene.

The reaction mixture, which is a viscous brown mass, is transferred to a flask, the autoclave is washed out with 30 g of toluene, and the washings are added to the mixture, which is then fractionally distilled. After the toluene has been distilled off in vacuum, 215 g of a product boiling at 129-134°/24-25mm is obtained, leaving 65 g of tarry residue. Redistillation gives 190.2 g of vinylcaprolactam, b.p. 131-132°/22 mm. Extraction of the tarry product with ether gives a further 9.2 g of vinylcaprolactam, b.p. 129-130°/20.5 mm, giving a total yield of vinylcaprolactam of 199.4 g, or 71%, calculated on the amount of ϵ-caprolactam taken (226 g). Part of the vinylcaprolactam obtained was distilled, using a laboratory column, type LKS, height of working section 600 mm, filled with glass rings of diameter 1.5 mm (15-20 theoretical plates). This distillation confirmed the purity of our product, which had the following constants: b.p. 95°/4 mm; d_4^{40} 1.0084; n_D^{40} 1.5051; found MR_D 40.890.

$C_8H_{13}NO$.	Calculated MR_D (for N-vinyl)	40.428
	Calculated MR_D (for O-vinyl)	40.795

Vinylcaprolactam is a colorless crystalline substance, m.p. 34-35°, with, however, a tendency towards remaining in the liquid state even when pure; rapid crystallization may be induced by mechanical factors, and is associated with evolution of heat. The substance is readily soluble in ether, ethanol, benzene, toluene, and gasoline.

Found %:	C 68.76; 69.10; H 9.17; 9.30
$C_8H_{13}NO$. Calculated %:	C 69.06; H 9.42
Found %:	N 10.00; 9.82
$C_8H_{13}NO$. Calculated %:	N 10.07
Found M	138.50; 139.63
$C_8H_{13}NO$. Calculated M	139.11

Hydrolysis of vinylcaprolactam

1. Two sealed bulbs each containing 20 ml of 4.5% sulfuric acid and 0.1954 or 0.2054 g of vinylcaprolactam were heated for 55 hrs. at 55-60°, well cooled before opening, and the contents were transferred quantitatively to 25 ml of a cooled solution of sodium bisulfate. Acetaldehyde formed was determined iodometrically after 30 min., by Ripper's method.

% Hydrolysis of vinylcaprolactam: (a) 81.1 (b) 78.7

2. Bulbs containing (a) 0.1031 (b) 0.1028 g of the substance, with 20 ml of 4.5% sulfuric acid in each, were heated in a thermostat for about 10 hrs at 80°, followed by 35 hrs at 110°; further treatment was as in Experiment 1.

% Hydrolysis of vinylcaprolactam: (a) 15.3 (b) 14.7.

3. (a) 10.01 g of vinylcaprolactam and 450 ml of 4.5% sulfuric acid were heated at 60° for 23-25 hrs in a flask fitted with a stirrer, a thermometer, and a condenser, connected with two cylinders containing sodium bisulfite solution; the final volume of the solution was 446 ml. 25 ml of bisulfite solution was added to 10 ml of the reaction mixture, and % hydrolysis was measured; it amounted to 63.2.

Alkali was added to the remaining solution until it had only a weakly acid reaction, and water was evaporated off under reduced pressure. Benzene extraction of the residue gave 0.2 g of a substance melting at 64-69°, shown to be caprolactam (no depression of m.p. of a known sample).

(b) 5 g of caprolactam and 50 ml of 4.5% sulfuric acid were heated under reflux in a round-bottomed flask for 20 hrs at 60°. Alkali was then added to a weakly acid reaction, water was eliminated under reduced pressure, and the residue was dried to constant weight (9.9 g). 1.5 g of caprolactam was extracted from the residue with benzene.

Polymerization of vinylcaprolactam

1. 7.1 g of vinylcaprolactam and 0.07 g of benzoyl peroxide were heated in a bulb for 40 hrs at 55-60°. Distillation of the mixture gave 7 g of the initial vinylcaprolactam, with a small amount of tarry matter.

2. 15.7 g of vinylcaprolactam and 0.25 g of 25% hydrogen peroxide were heated in a bulb for 10 hrs at 80°, and then for about 40 hrs at 110°. The reaction mixture, a brown liquid, was dissolved in gasoline, and the precipitated resin was repeatedly treated with gasoline, finally to give a small amount of a yellow powder, which was soluble in benzene, ethanol, and cold water, from which it is precipitated by heating. The yield of polymer was 1.5 g, being 1% of the amount of vinylcaprolactam taken. The polymer was reprecipitated from benzene solution.

Cryoscopic determination of molecular weight in benzene solution gave values of 871 and 1024.

The solution remaining after precipitation of the polymer was fractionally distilled in vacuum, after distilling off the solvent. The products were (a) vinylcaprolactam, b.p. 138-141°/31-33 mm, 9.7 g, (b) impure vinylcaprolactam, 1 g, and (c) tarry residue.

3. 31 g of pure vinylcaprolactam (b.p. 103-104°/5.5-6 mm) in a round-bottomed flask fitted with a stirrer, a thermometer, and a reflux condenser, was heated to 140°, and 32% hydrogen peroxide was added drop by drop during 19 hrs, a total of 0.77 g of hydrogen peroxide being added, or 2.4% of the amount of vinylcaprolactam. The reaction mixture was a brown, viscous liquid, from which 12 g of polymer was precipitated as a yellow powder by addition of ether. The filtrate gave a further 2.5 g of polymer, in the form of a semi-liquid resin, and 14 g of monomer, and reprecipitation of the resin gave 1.3 g of solid polymer, the total yield of which was thus 13.3 g, or 42.9% of the vinylcaprolactam taken. Redistillation of the 14 g of monomer recovered from the reaction mixture was associated with further polymerization, yielding 6 g of solid polymer, the total yield of which was thus raised to 19.3 g, or 62.2%.

4. 27 g of vinylcaprolactam was heated for 18-19 hrs at 140-150° with 0.5 g of catalyst in the apparatus described above. The catalyst was prepared by heating vinylcaprolactam with hydrogen peroxide, and is a crystalline substance. The reaction mixture was a dark brown liquid, from which 14 g of polymer was obtained by adding 200 ml of ether, this being a yield of 51.4%. The molecular weight of polymer precipitated from benzene by addition of ligroin was determined cryoscopically in benzene solution, values of 2855 and 2655 being obtained.

Polyvinylcaprolactam is a faintly yellow powder, readily soluble in cold water, benzene, and ethanol, and insoluble in ligroin and ether. It separates out from its aqueous solutions when they are warmed.

Product of reaction of vinylcaprolactam with hydrogen peroxide

32% Hydrogen peroxide (0.28 g) is added gradually to 34 g of vinylcaprolactam in a flask fitted with a reflux condenser, a stirrer, and a thermometer, at 100°; the temperature is raised during the first 90 min. to 150°, and then during the next hour to 170°. The crystalline product is cooled and extracted with ether, to separate it from the small amount of polymer formed, the ether is distilled off, as is unreacted vinylcaprolactam (16 g); owing to which the crystalline product dissolved in ether. When distilling off the ether we observed formation of a white deposit on the walls of the receiver, indicating that the crystalline product is somewhat volatile. The residue after distilling off monomer (12.1 g) is a viscous oil, treatment of which with ether gives 8 g of white crystalline substance, soluble in benzene and ethanol, sparingly soluble in water, ligroin, light petroleum, and ether. After recrystallization from hot water or light petroleum it melts at 144-145°.

Determination of molecular weight (cryoscopic method)

Found M: a) 309; b) 314; mean 311
Calculated for $C_{16}H_{26}N_2O_4$; M 310

The substance reacts as a peroxide, and acts as an initiator of the process of polymerization of vinylcaprolactam.

SUMMARY

1. A method for obtaining vinylcaprolactam in about 70% yield was found.

2. A new catalyst was used for vinylation of ϵ-caprolactam, viz., "the potassium salt of ϵ-caprolactam" (the product of reaction of potassium with ϵ-caprolactam).

3. Vinylcaprolactam is readily obtained in crystalline form; this is highly hygroscopic, and it absorbs an equimolecular amount of water when exposed to the air.

4. Hydrolysis of vinylcaprolactam gives acetaldehyde, ϵ-caprolactam, and salts of ϵ-aminocapronic acid.

5. Polymerization of vinylcaprolactam proceeds satisfactorily in presence of hydrogen peroxide at 140-150°.

6. A crystalline intermediate product of polymerization of vinylcaprolactam was isolated. It is formed by the action of oxygen on vinylcaprolactam, and it exhibits peroxide properties, and can serve as an initiator of the polymerization process.

7. The process of thermopolymerization of vinylcaprolactam proceeds only to a negligible extent.

Received January 14, 1952

Institute of Organic Chemistry
Academy of Sciences USSR

LITERATURE CITED

[1] V. V. Korshak, Chemistry of High-Molecular Compounds, U.S.S.R. Acad. Sci. Press, 1950.

[2] A. E. Favorsky, J. Russ. Phys. Chem. Soc. 19, 414 (1888); 20, 518 (1889); A. E. Favorsky and M. F. Shostakovsky, J. Gen. Chem., 13, 1 (1943); A. E. Favorsky and M. F. Shostakovsky, Authors certif, 59308 (1941); A. E. Favorsky, V. I. Ivanov, and Z. I. Kuznetsova, Proc. Acad. Sci. USSR, 32, 630(1941); M. F. Shostakovsky, J Gen. Chem., 20, 608 (1950)*; M. F. Shostakovsky, E. N. Prilezhayeva, and E. S. Shapiro, Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 3, 284 (1951); No. 4, 438 (1951); M F. Shostakovsky and F. P. Sidelkovskaya, J. Gen. Chem., 21, 1610 (1951)**; M. F. Shostakovsky and A. V. Bogdanova, J. Gen. Chem., 21, 388, 394 (1951)***; M. F. Shostakovsky, and N. A. Gershtein, J. Gen. Chem., 21, 1453, 1602 (1951).****

---

* - **** See next page.

[3] M. F. Shostakovsky, I. A. Chekulaeva and N. A. Gershtein. Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 3, 328 (1951); M. Koton, P. Mulyar, N. Radinskaya, and B. Yakovlev, J. Appl. Chem., 3, 10 (1948); Final report 359; W. Handford, D. Fuller, Ind. Eng. Chem., 40, 1171 (1948); U.S. Pat. 2231905. Chem. Abs. 3267, 4, (1941); US Pat. 2317804; Chem. Abs. 6057 (1943); British Pat. 792391 (C. 13410)(1936); German Pat. 618120; Chem. Abs. 883 (1947); Kline, Mod. Plast. 24, No. 3, 157-158, 194 (1946); Final report 266 (BIOS); G. Jones, I. Lomfeler, K. Hawking, J. Org. Chem., 9, 500 (1944); Chem. Abs. 1134 (1945).

[4] Final report No. 354, No. 266 (BIOS); Gordon Kline, Mod. Plast. 23, No. 3, 157-161, 212-218 (1945); Chem. Abs. 2033 (1946); Barfur Eichler, Arch. exp. Path. Farm. 206, 346 (1949); Chem. Abs. 8543 (1949); German Pat. 738994, Chem. Abs, 5408 (1945); Ann. Pharm. Franc. 5, 93 (1937); Chem. Abs. 286 (1948).

[5] US. Pat. 2317804 (1943).

[6] O. Wallach, A 312, 188 (1900).

[7] R. Benson, T. Cairns, J. Am. Chem. Soc., 70, 2115 (1948); Chem. Abs., 6749 (1948).

[8] M. F. Shostakovsky. Authors certificate No. 64331 (1945).

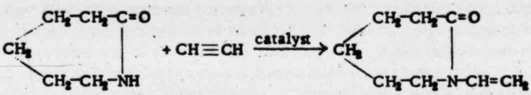
* See Consultants Bureau English Translation, p. 643.
** " " " " " p. 1767.
*** " " " " " p. 429, p. 435.
**** " " " " " p. 1581, p. 1757.

SYNTHESIS AND TRANSFORMATIONS OF VINYLCAPROLACTAM

PART 1. POLYMERIZATION IN PRESENCE OF HYDROGEN PEROXIDE

M. F. Shostakovsky, F. P. Sidelkovskaya, and M. G. Zelenskaya

N-Vinylcaprolactam is a compound of considerable interest; it may be prepared from caprolactam and acetylene in presence of alkaline catalyst [1]:



In the given case, as in that of vinylation of hydroxy-compounds [2], undiluted acetylene gives good yields. Favorsky and Shostakovsky [2] successfully applied undiluted acetylene to synthesis of vinyl ethers of the type $CH_2=CH-OR$, as long ago as 1943; in spite of this, foreign workers still use acetylene diluted with inert gases for the purpose [3], although Favorsky and Shostakovsky's method is generally and widely applied in the Soviet Union.

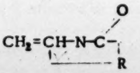
A method for production of vinylcaprolactam has recently been worked out in our laboratory [1], by heating caprolactam with acetylene, in toluene solution, with potassium salt of caprolactam as catalyst. The preparation of this catalyst presents, however, certain difficulties, associated with the use of metallic potassium, which so readily reacts with oxygen, with inflammation, on exposure to the air. Additional researches were undertaken in order to find a more readily prepared catalyst than the caprolactam salt, such as, in particular, potassium hydroxide. Although it was evident from preliminary experiments [1] that this catalyst did not give the desired results, it was nevertheless thought desirable to subject this catalyst to a more detailed examination. Potassium hydroxide was added either immediately before vinylation, or it was previously heated with caprolactam in an autoclave; in the latter case heating was at atmospheric pressure or at 150 atmospheres. Synthesis of vinylcaprolactam did not take place under any of these conditions.

Since potassium salt of caprolactam could not be replaced by potassium hydroxide, we next studied the effect of substituting metallic sodium for potassium, as being more convenient to handle. The sodium salt was found to be as effective a catalyst as is the potassium salt of caprolactam, the yields of vinylcaprolactam being 70-80% in both cases (see Experimental Section, below).

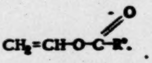
The reaction of vinylation was conducted using different solvents, viz., toluene, vinyl butyl ether, ligroin, and butanol. The reaction proceeds similarly in the first three solvents, the only differences being in the isolation and purification of the product. In the last case, it was thought that conjugated vinylation of caprolactam and of the solvent might take place, analogous to oxidation of difficultly oxidizable substances in presence of readily oxidized ones [4].

In spite, however, of variation of the reaction conditions (temperature, catalysts), vinylcaprolactam was not obtained, and vinyl butyl ether was only obtained in one case (temperature 140°, KOH catalyst) in small yield. It is evident that the simultaneous presence of caprolactam and butanol somehow leads to inhibition of the reaction of vinylation of both substances. We now recommend vinylation of caprolactam in ligroin solution, with its sodium salt as catalyst.

Vinylcaprolactam may be regarded as having the structure:



where R is a bivalent radical. In this respect it may be considered as an analog of vinyl esters of type (I), but not of ethers of type (II):



$CH_2=CH-O-C(=O)-R^{\bullet}$. (I)

$CH_2=CH-O-R^{\bullet}$ (II)

As could be expected from a consideration of the structure of vinylcaprolactam it has a tendency towards polymerization. It is relatively stable at ordinary temperatures, but it partly polymerizes when heated (100-150°), and gives high yields of polymer in presence of hydrogen peroxide [1]. The present research is devoted to the study of polymerization of vinylcaprolactam at different temperatures, in presence of the given catalyst; the results are shown in Table 1.

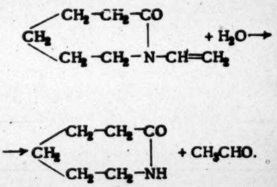
It appears from Table 1 that the velocity of polymerization falls parallel with temperature, and the amount of catalyst required rises. The optimum temperature is 140-150°, at which 33 g of vinylcaprolactam undergoes polymerization during 7-9 hrs, with yields of about 70%. At 100-125° polymerization of about the same amount of vinylcaprolactam proceeds only to about 25-50% after 22-23 hrs. It also follows from the data of Table 1 that a relatively small change in temperature causes a fairly considerable change in the velocity of polymerization, with only slight change in the properties of the polymer. The specific viscosity of the polymers obtained over the range 100-150° is $\eta_{sp.} = 0.11-0.17$ (1 g/100 ml of benzene), and the mean molecular weight, determined cryoscopically in benzene, is 1000-1500.

It is of interest that at 100-125° acetaldehyde and caprolactam were formed together with the polymer. It is quite probable that the small amount of water introduced with the hydrogen peroxide was sufficient for effecting partial hydrolysis of vinylcaprolactam:

TABLE 1

Polymerization of vinylcaprolactam in presence of H_2O_2 (29% solution)

Expt. No.	Temp. °C	Duration in hours	Amount of 29% H_2O_2 solution, in g	Amount of polymer formed, as % of vinylcaprolactam taken	Amount of unreacted monomer, %	Mol. wt. (cryoscopically, in benzene)	$\eta_{sp.}$ (1 g in 100 ml benzene)
3	140-143	7	0.45	70	21	1602; 1715	0.1740
4	143-147	9	0.64	68.4	25.8	1209; 1070	0.1673
5	143-149	9	1.20	72.4	18.7	1235; 1394	0.1417
7	115-125	22	1.90	24.5	18.6*	Sparingly soluble in C_6H_6	0.1109
8	100-105	23.5	2.00	50	12.2*	–	0.1133



---

* Caprolactam and acetaldehyde were formed as well as polymer in these experiments.

EXPERIMENTAL

A. Vinylation of caprolactam in benzene solution

Catalyst: sodium salt of caprolactam.

a) Preparation of catalyst. 40 g of caprolactam and 1.86 g of sodium finely dispersed by Bruhl's method [7] in 50 ml of ligroin (b.p. 130-150°) are heated with constant stirring to complete dissolution of the sodium, which takes about an hour.

b) Vinylation is effected as usual in a rotating stainless steel autoclave. 45 g of caprolactam and 150 ml of ligroin (b.p. 100-120°) are added to the product obtained above, and the mixture is placed in a 2500 ml autoclave; the total charge was: caprolactam 77 g, Na salt of caprolactam 10 g, and ligroin 200 ml. The autoclave is filled with acetylene at a pressure of 15-18 atm., and the temperature is raised to 115-125°. The autoclave is then allowed to cool, a fresh charge of acetylene is added, and the autoclave is again heated. This operation is repeated until somewhat more than the theoretical amount of acetylene has been absorbed. The mixture is then filtered, and the precipitate (16.3 g) is washed with five portions of ligroin. The solvent is distilled off from the filtrate + washings, at ordinary pressure, and the residue is fractionated under reduced pressure, to give 75.2 g (79.8% yield) of vinylcaprolactam, b.p. 119-121°/13 mm, n_D^{20} 1.5139, redistillation of which affords 73.8 g of product, b.p. 104-105.5°/7-7.5 mm; n_D^{20} 1.5138.

B. Polymerization of vinylcaprolactam

1. At 140-150°. 0.16 g portions of catalyst (29% aqueous H_2O_2) are added at 1½-2 hrs intervals, to a total of 1.20 g, to 32.6 g of vinylcaprolactam in a flask fitted with a mechanical stirrer, a thermometer, and a reflux condenser, immersed in an oil bath at 143-144°. Addition of each of the initial portions of catalysts was followed by a temperature rise of 15-20°, but the final portions gave hardly any thermal effect. The total duration of the process is 9 hrs, at an average temperature of 140-150°. The final reaction mixture is a light brown viscous liquid, which changes to a vitreous solid on cooling. Repeated extraction of this with dry ether gives 23.8 g of amorphous polymer of vinylcaprolactam, representing a yield of 72.4%, calculated on vinylcaprolactam taken for the reaction, or of 90% calculated on the amount actually reacted. Fractionation of the ether extracts gives 6.1 g of unreacted vinylcaprolactam, b.p. 104-107°/7 mm, and 2.3 g of vitreous polymer*.

TABLE 2

Data for fractionation of ethereal extracts of the polymerization product

Extract No.	Volume, ml	Amount of monomer, g	Amount of polymer, g
1	50	2.27	1.06
2	50	1.66	0.66
3	50	1.65	0.57
4	50	0.51	–
Total	200	6.09	2.29

The results of fractionation of the individual extracts are given in Table 2, from which it appears that the content of monomer is greatest in the first extract, and is very small in the fourth one; the polymer content falls in the same order. It is evident that the presence of monomer in the ether raises the solubility in it of the polymer.

The powdery polymer is dried in a vacuum desiccator to constant weight; its specific viscosity and molecular weight are: $\eta_{sp.} = 0.1417$ (1 g/100 ml of benzene); M = 1293; 1394 (cryoscopically, in benzene).

2. At 115-125°. The reaction is conducted in the same apparatus as before, with the difference that the reflux condenser is connected to a series of three Tishchenko wash bottles, in order to absorb any acetaldehyde formed. 28% Hydrogen peroxide is added to 32.2 g of vinylcaprolactam at 115-125°, in small portions, as before. Only a slight temperature rise is observed (2-3°) when the catalyst is added, in this case. The reaction product remains liquid for a very long time, and only after 22 hrs, and addition of 1.88 g of peroxide does it assume the consistency of a viscous resin. The product smells strongly of acetaldehyde, and it gives a positive reaction with fuchsin-bisulfite reagent. The reaction product is extracted with 5 portions of ether, giving 5.9 g of powdery polymer. The solvent is distilled off from the ethereal extracts, collecting the fraction boiling at 34-36°, and repeatedly extracting it with water. Titration of an aliquot part of the aqueous extract with sodium bisulfite gave 0.4 g of acetaldehyde, corresponding to 1.4 g, or to 4.3% of the vinylcaprolactam initially taken.** The tarry residue left after distilling off the ether was fractionated in vacuum, giving:

1) vinylcaprolactam (b.p. 98-99°/5 mm; n_D^{20} 1.5130) –6 g; (18.6%);
2) caprolactam (m.p. 60-62°, after recrystallization from ethanol 67-69°) –3.75 g (14.3%) ***;
3) resinous polymer –3.5 g, from which 2 g of powdery polymer was obtained by reprecipitation. The total yield of powdery polymer is thus 7.9 g, i.e. 24.5 %.

Description of the polymer. The polymer is partly soluble in benzene. 2.91 g of polymer is treated with 20 ml of dry benzene, the residue is filtered off, and 80 ml of dry ether is added to the filtrate. The powdery precipitate is collected, washed with ether, and dried, giving 1.83 g of polymer($\eta_{sp.} = 0.1109$) (1 g of polymer in 100 ml of benzene); M = 2618; 2364 (cryoscopic method, in benzene).

---

*Further studies showed that the vitreous product is a mixture of the pure powdery polymer with monomer. It is not possible, in working with small amounts of vitreous polymer, to effect a satisfactory separation into its two components, since during reprecipitations a considerable part of the polymer remains in solution, under these conditions.

** Since it is not possible to recover all of the acetaldehyde forming during the reaction, percentage hydrolysis is calculated from the amount of caprolactam found.

*** The yield of reaction products is expressed as percentages of the amount of vinylcaprolactam taken for the reaction.

3. At 100-110°. The apparatus and methods were as in Experiment 2. 28% peroxide is added to 24.5 g of vinylcaprolactam at 100-105°, and the temperature is maintained at 100-110° for 23½ hours, during which time 2 g of catalyst is added, in all. Heating is then stopped, and a stream of nitrogen is passed through the system. Both the viscous polymerization product and the water in the wash bottles have a strong smell of acetaldehyde, and give a positive reaction with fuchsin reagent. Titration with sodium bisulfite of an aliquot part of the basic product gives an acetaldehyde content of 0.2 g, and of the water in the wash bottles a further 0.52 g, making 0.72 g in all. This corresponds with hydrolysis of 2.3 g of vinylcaprolactam.

Further confirmation of the presence of acetaldehyde in the wash bottle water was afforded by preparing its 2,4-dinitrophenylhydrazone, m.p. 162.5-163.5°, after recrystallization from ethanol.

The resinous basic reaction product is treated as in Experiment 2, giving:

(1) powdery polymer - 12.1 g (50%);
(2) unreacted monomer - 3 g (12.2%);
(3) caprolactam - 5.4 g, corresponding to 6.6 g of vinylcaprolactam (27%).

The polymer is soluble in benzene, and its viscosity $\eta_{sp.}$ = 0.1133 (1 g of polymer in 100 ml of benzene).

SUMMARY

1. The preparation of vinylcaprolactam from acetylene and caprolactam is described; the sodium salt of caprolactam serves as a quite satisfactory catalyst.

2. Polymerization of vinylcaprolactam in presence of hydrogen peroxide has been studied over the range 100-150°. The velocity of polymerization rises, and the amount of catalyst required falls, as the reaction temperature is raised.

Received January 14, 1952

Institute of Organic Chemistry
Academy of Sciences USSR

LITERATURE CITED

[1] M. F. Shostakovsky, N. A. Medzykhovskaya, and M. G. Zelenskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 4, 682 (1952). (See Consultants Bureau English Translation, p. 627 ff.)

[2] A. E. Favorsky and M. F. Shostakovsky, J. Gen. Chem., 13, 1 (1943).

[3] J. Copenhaver, Acetylene and Carbonoxide chemistry, 1949.

[4] A. N. Bakh, Selected works, p. 82. Leningrad, 1937.

[5] M. F. Shostakovsky, Herald Acad. Sci. USSR, No. 12, 13 (1948).

[6] M. F. Shostakovsky, Studies in the field of high-molecular compounds, p. 34. Moscow-Leningrad, 1949.

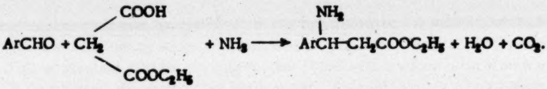
[7] J. Bruhl, Ber., 37, 2067 (1909).

NEW SYNTHESIS OF ALKYL ESTERS OF β-AMINO-ACIDS

V. M. Rodionov and N. N. Bezinger

The new synthesis of β-amino-acid esters depending on reaction of aromatic aldehydes with malonic mono-ester in the presence of ammonia was undertaken because of the belief expressed in the older literature that the usual method cannot be applied to the preparation of β-amino-acids, as their tendency towards deamination would lead to the obtaining of very low yields. It was found later that this view is not always justified, since the deamination reaction was found to depend on the nature of the alkyl (or aryl) residue of the β-amino-acid, and on its structure. In many cases alkyl esters can be obtained in very good yield by heating alcoholic solutions of β-amino-acids with small amounts of concentrated sulfuric acid.

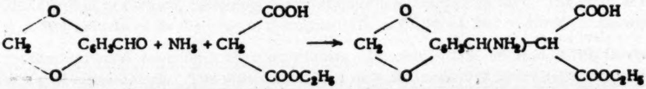
The method worked out for the synthesis of esters of β-amino-acids does not differ basically from that proposed by Rodionov and Malevinskaya [1] for the synthesis of β-amino-acids, or from the method for preparation of esters of β-aminoisosuccinic acid [2], i.e., the reaction proceeds according to the following general equation:



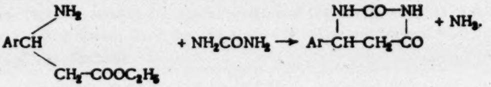
$$ArCHO + CH_2(COOH)(COOC_2H_5) + NH_3 \longrightarrow ArCH(NH_2){-}CH_2COOC_2H_5 + H_2O + CO_2.$$

The alkyl esters of β-aryl-β-amino-acids are obtained in yields of 35-45% , and esters of arylacrylic acids are formed in yields of 40-45% . The ethyl esters of β-phenyl-β-alanine, β-piperonyl-β-alanine, and β-(3-nitrophenyl)-β-alanine were obtained by this method.

It is of particular interest that when piperonal is condensed with monoethyl malonate under mild conditions simultaneous decarboxylation does not take place, the product being monoethyl β-piperonyl-β-amino-isosuccinate. This confirms the correctness of the reaction mechanism:



Experiments were performed on the synthesis of ureido-derivatives of the esters obtained, in order to assist in their identification. The esters do not react with urea, however, to give the expected esters of β-ureidoacids, dihydrouracils being obtained instead. The reaction proceeds very readily, the dihydrouracils being obtained in good yield from the esters and a boiling aqueous solution of urea:



$$ArCH(NH_2){-}CH_2{-}COOC_2H_5 + NH_2CONH_2 \longrightarrow Ar{-}\underset{|}{CH}{-}CH_2{-}CO\ (NH{-}CO{-}NH) + NH_3.$$

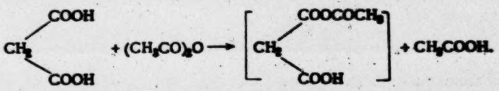
We know that free ureido-acids are converted into dihydrouracils with some difficulty, requiring boiling with hydrochloric acid.

The preparation of certain alkyl esters of β-amino-acids by the classical method is also described in this paper.

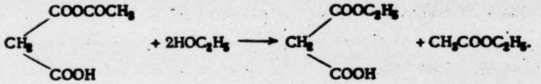
EXPERIMENTAL

Preparation of monoethyl malonate. There are two methods for preparation of monomethyl malonate. One, which was suggested by Van t'Hoff [3], and was worked out by Freund [4], consists of cautious hydrolysis of the diethyl ester with alcoholic caustic potash; the ethyl potassium salt crystallizes out in well-formed platelets after long standing of the solution. The crystals are treated with hydrochloric acid, and the solution is extracted with ether. The ether extract is dried with anhydrous sodium sulfate, the ether is distilled off, and the residue is dried at room temperature in a vacuum desiccator over anhydrous Na_2SO_4, giving monoethyl malonate in 80% yield.

The second method was worked out by Vulfson [5]. Well dried malonic acid is dissolved in acetic anhydride (1:2 mol), and 24 hrs later excess of absolute ethanol is added, and the mixture is boiled for 1 hr. and then vacuum distilled, giving a 40% yield of monoethyl malonate. Vulfson supposes that the reaction proceeds according to the scheme:



The anhydride of malonic and acetic acids is unstable, and it reacts with ethanol giving ethyl acetate and monoethyl malonate:



We at first used Vulfson's method, but owing to its low yields we later on transferred to Van t'Hoff and Freund's method.

Preparation of monoethyl malonate by hydrolysis of diethyl malonate. A solution of 26.1 g of KOH in 300 ml of absolute ethanol is added drop by drop, with constant stirring, to a solution of 75 g of freshly distilled diethyl malonate in 300 ml of absolute ethanol, in a liter flask fitted with a stirrer with a mercury seal, and stirring is continued for 2 hrs after all the reagent has been added. A small amount of potassium malonate separates from the solution during the reaction, and is separated by bringing the solution to the boil, and filtering the hot solution. Large crystals of ethyl potassium malonate are deposited from the cooled filtrate, and they are collected on the filter, washed with dry ether, and dried in a vacuum desiccator; yield 68 g, or 85%.

68 g of ethyl potassium malonate is dissolved in 35 ml of water, and concentrated hydrochloric acid is added at 0°, with constant stirring, until the solution becomes acid to Congo red, when it is repeatedly extracted with ether. The ethereal extract is dried with anhydrous Na_2SO_4, the ether is distilled off, and the residue is fractionally distilled in vacuum, collecting the fraction of b.p. 100-101°/4 mm. The yield of monoethyl malonate is 50.7 g, or 96% calculated on the basis of potassium salt, or 81.9% on that of diethyl malonate taken.

Synthesis of ethyl β-amino-β-phenylpropionate. 10 ml of a 15% solution of NH_3 in absolute ethanol is added to 12 g of benzaldehyde. The white precipitate of hydrobenzamide which separates when the first few ml of ammonia are added goes back into solution when the rest of the reagent is added. 11 g of monoethyl malonate is then added, this being associated with evolution of considerable heat, and the mixture is then heated at 100° until all the ethanol has distilled off, and until evolution of CO_2 has ceased (10 hrs). The resulting brown oil is treated with an equal volume of water, and the aqueous layer is extracted repeatedly with small portions of ether. The ethereal extracts are added to the oil residue, and the mixture is dried with anhydrous Na_2SO_4. Long colorless needles separate from the residue during evaporation of the ether, which is continued until the volume of the solution is 1/3 of the initial value, when the precipitate is collected, washed with ether, and dried; 0.09 g of product, m.p. 144-145°, is obtained.

Found %: C 73.52; H 6.01; N 9.50
C_9H_9ON. Calculated %: C 73.44; H 6.16; N 9.52

The analytical results, and the properties of the product, correspond with cinnamamide, which, according to the literature, has m.p. 146-147°.

The mother liquor from the cinnamamide is dissolved in twice its volume of ether, and the solution is saturated with dry HCl, cooling in a freezing mixture. A yellow oil which at first separates solidifies later on. The hydrochloride of ethyl β-amino-β-phenylpropionate is collected, and washed with absolute ethanol, to remove HCl. The yield is 9.8 g, m.p. 137-147°. The product is soluble in hot ethanol, and insoluble in cold ethanol, ether, and water.

Attempts at purifying the hydrochloride were unsuccessful, the m.p. remaining indefinite after three recrystallizations (139-146°). We were not able to find any reference to the m.p. of this hydrochloride in the literature.

Posner found that β-phenyl-β-alanine formed, in addition to the ordinary monohydrochloride, an acid hydrochloride with 3 molecules of HCl, which was stable at the ordinary temperature, but evolved HCl when heated, and it may be that we obtained a mixture of the normal and the acid hydrochlorides; hence the indefinite m.p. of our product.

9 g of hydrochloride is made up into a paste with a little water, and 3% aqueous $NaHCO_3$ is added in small portions, with energetic stirring, giving a heavy, colorless oil. The supernatant aqueous layer is extracted with two portions of ether, and the extract is added to the oil, the solution then being dried with anhydrous Na_2SO_4. The ether is evaporated off in vacuum, and the residue is fractionally distilled, collecting the fraction boiling at 116-119°/7 mm, which is redistilled, when 7.2 g (45% yield calculated on monoethyl malonate taken) of ester is obtained. Ethyl β-phenyl-β-alanine, b.p. 116-117°/7 mm, is a syrupy colorless liquid with a fairly pleasant odor.

Found %: N 7.08; 7.15
$C_{11}H_{15}O_2N$. Calculated %: N 7.25

Synthesis of ethyl β-amino-β-piperonylpropionate. 15 ml of a 15% solution of ammonia in absolute ethanol and 9.3 g of monoethyl malonate are added to 10.4 g of piperonal dissolved in a small volume of ethanol. Considerable heat is evolved, with vigorous production of CO_2. The mixture is heated on the water bath until all the alcohol has distilled off, and until evolution of CO_2 ceases (15 hrs). The final product is a dense brown liquid, which is treated with twice its volume of hot water, and the aqueous layer is extracted with ether. The extract is added to the oily product, and the solution so obtained is dried with anhydrous Na_2SO_4.

The dried solution gradually deposits a colorless crystalline product, which is collected, washed with cooled ether, and dried; yield 0.55 g, m.p. 69-70°, readily soluble in ether and acetone, sparingly soluble in ethanol, insoluble in water or aqueous sodium carbonate. The alcoholic solution decolorizes bromine water or $KMnO_4$ solution. The product does not contain nitrogen.

Found %: C 65.61; H 5.30
$C_{12}H_{12}O_4$. Calculated %: C 65.44; H 5.49

The product is ethyl β-piperonylacrylate, whose m.p. is reported in the literature as 67-68° [5].

Saturation with dry HCl of the mother liquor from this product, with cooling in a freezing mixture, gives a yellowish precipitate of the hydrochloride of the ethyl ester of β-piperonyl-β-alanine, which is collected, washed free of HCl with absolute ethanol, and dried; yield 9.3 g, m.p. 182-183°.

8 g of hydrochloride is treated with 3% $NaHCO_3$ solution, at 0°, giving 7.5 g of ethyl ester of β-piperonyl-β-alanine, a yield of 45% calculated from monoethyl malonate taken, or of 69.8% calculated from hydrochloride taken. The syrupy product crystallizes after a few days, and the ester is recrystallized from ethanol, m.p. 70-71.5°. The ethyl ester of β-piperonyl-β-alanine is soluble in hot ethanol and ether, but not in water, alkalis, or acids.

Found %: N 5.81; 5.80
$C_{12}H_5O_4N$. Calculated %: N 5.90

A precipitate of some unknown substance was observed to form during the reaction, and then to disappear as the reaction proceeded towards completion. The reaction was repeated with certain modifications, in order to discover the nature of this product. Heating of the reaction mixture was not continued until no more CO_2 was evolved, but was stopped when the amount of precipitate appeared to be at a maximum. The precipitate was found to be an intermediate product of condensation of aldehyde with monoethyl malonate, viz., monoethyl β-amino-β-piperonylisosuccinate.

A mixture of 17.5 g of piperonal, 19 g of monoethyl malonate, and 25 ml of 15% NH_3 in absolute ethanol was heated on a boiling water bath until all the ethanol had evaporated (5 hrs), although CO_2 was still being evolved. The reaction mixture then consisted of a dense brown liquid, with a considerable amount of white crystalline precipitate. It was treated with ether, which dissolved only the oily part, leaving the crystalline product, which is collected, washed with ether, and dried in a vacuum desiccator; yield 4.39 g, m.p. 115-116° (decomp.). The product decomposes when heated, with evolution of CO_2 and NH_3.

Found %: N 5.14; 5.16
$C_{13}H_{15}O_6N$. Calculated %: N 4.98

As in the preceding experiment, the ethereal extract was concentrated to a third of its volume, in order to obtain ethyl piperonylacrylate, which was not, however, formed. An equal volume of dry ether was then added, and the solution was saturated with dry HCl, giving 2.1 g of the hydrochloride of the ethyl ester of β-piperonyl-β-alanine.

Synthesis of ethyl β-amino-β-3-nitrophenylpropionate. A mixture of 13.1 g of m-nitrobenzaldehyde, 10.8 g of monoethyl malonate, and 15 ml of 15% alcoholic ammonia is heated on a boiling water bath until evolution of CO_2 ceases (10 hrs). A yellow precipitate forms at the beginning of the process, but disappears after two hours of heating. The brown oil obtained at the end of the reaction is treated with twice its volume of hot water, and the aqueous extract is extracted with a few small portions of ether; the ethereal extract is then added to the residual oil, the solution is dried with anhydrous Na_2SO_4, and saturated with dry HCl. The yellow oil which separates soon crystallizes; it is collected, washed with dry ether, and dried, giving 10.1 g of the hydrochloride of the ethyl ester of β-(3-nitrophenyl)-β-alanine, m.p. 171-172°, insoluble in ether or cold ethanol, readily soluble in hot ethanol; yield 51.6%, calculated on monoethyl malonate taken.

10 g of the hydrochloride is treated with 3% $NaHCO_3$ solution at room temperature, when a yellow oil is obtained. This is separated, the aqueous layer is extracted a few times with ether, and the extracts are added to the oil. The resulting solution is dried with anhydrous Na_2SO_4, the ether is evaporated off in vacuum, and the residual oil is cooled in ice water, when it crystallizes, giving 8.1 g of ethyl ester of β-(3-nitrophenyl)-β-alanine, m.p. 77-78°, yield 93% calculated on hydrochloride taken, or 44.6% calculated on monoethyl malonate taken.

Found %: C 55.61; 55.39; H 6.00; 5.73; N 11.56; 11.60
$C_{11}H_{14}O_4N_2$. Calculated %: C 55.45; H 5.92; N 11.76

Preparation of 4-phenyldihydrouracil. 3 g of urea in 15 ml of water is added to a solution of 1 g of ethyl ester of β-phenyl-β-alanine in 5 ml of ethanol, and the mixture is boiled under reflux until evolution of ammonia ceases (15 hrs). Thin silky needles separate from the cooled solution; they are collected, washed with water, and dried, giving 0.32 g of 4-phenyldihydrouracil, m.p. 216-218°, soluble in cold water, cold ethanol, or ether, readily soluble in hot ethanol. The mixed m.p. with a known specimen of 4-phenyldihydrouracil, prepared by a different method, was 218-220°.

Preparation of 4-piperonyldihydrouracil. A mixture of 1 g of ethyl ester of β-piperonyl-β-alanine in 5 ml of ethanol and 3 g of urea in 15 ml of water is boiled under reflux until evolution of NH_3 ceases (24 hrs). The cooled solution deposits a precipitate of small glistening platelets, which is collected, washed with water, and dried, giving 0.47 g of 4-piperonyldihydrouracil, m.p. 236-237°.

The published m.p. of this product is 247°, but repeated recrystallizations of our product failed to raise its m.p.

Found %: C 56.56; H 4.21; N 11.78
$C_{11}H_{10}O_4N_2$. Calculated %: C 56.40; H 4.30; N 11.96

Preparation of the ethyl ester of N-benzoyl-β-phenyl-β-alanine, by the classical method. 15.4 g of benzoyl chloride is added drop by drop, with constant stirring, to a solution of 16.4 g of β-phenyl-β-alanine in 170 ml of 10% caustic potash at ~0°; the temperature should at no time exceed 5°. The mixture is stirred for an hour after addition of the last drop of benzoyl chloride, and is then made acid with 1:1 hydrochloric acid. The product is collected on the filter, repeatedly washed with hot water, to remove benzoic acid, and recrystallized from boiling ethanol; yield 21.2 g (80% of theory).

20 g of N-benzoyl-β-phenyl-β-alanine is heated for 6-7 hrs under reflux on a boiling water bath with 100 ml of absolute ethanol and 4 ml of concentrated sulfuric acid, and about 50 ml of ethanol are then distilled off. The ethyl ester separates in the form of glistening needles from the cooled solution, and it is collected, washed, and dried. An equal volume of water is added to the filtrate, which is then made neutral with soda. The ethyl ester of N-benzoyl-β-phenyl-β-alanine which separates is collected, washed with water, and dried, and the combined precipitates are recrystallized from 50% ethanol; yield 18.9 g (~86% of theory), m.p. 112-113°.

Found %: N 4.80; 4.82
$C_{18}H_{19}O_3N$. Calculated %: N 4.72

The ethyl esters of N-benzoyl-β-(3-nitrophenyl)-β-alanine (yield ~ 92%) and of N-benzoyl-β-piperonyl-β-alanine (yield 82%) were obtained in the same way.

SUMMARY

1. A new method is described for the preparation of ethyl esters of β-aryl-β-aminoacids, depending on condensation of monoethyl malonate with aromatic aldehydes in the presence of alcoholic ammonia.

2. The method serves for preparation of the ethyl esters of β-phenyl-β-alanine, β-(3-nitrophenyl)-β-alanine, and β-amino-β-piperonylpropionic acid, and of monoethyl β-amino-β-piperonylisosuccinate.

3. The esters were converted into 4-aryldihydrouracils by boiling with urea solution.

4. Ethyl esters were prepared by the standard method from N-benzoyl derivatives of β-aminoacids.

Received March 25, 1952

LITERATURE CITED

[1] V. M. Rodionov and E. F. Malevinskaya, Ber. 58, 2952 (1926).

[2] V. M. Rodionov and A. M. Fedorova. Ber. 60, 1804 (1927).

[3] J. H. Van t'Hoff, Ber. 7, 1572 (1874).

[4] M. Freund, Ber. 17, 1780 (1884).

[5] N. Vulfson. J. Gen. Chem. 19, 1904 (1949). (See Consultants Bureau English translation, p. a-369.)

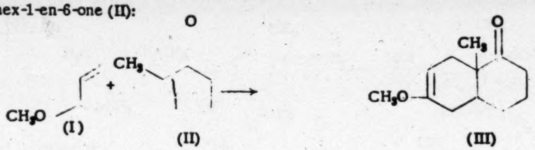
BLANK
PAGE

ACETYLENE DERIVATIVES

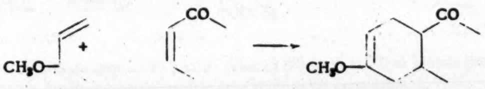
COMMUNICATION 127. SYNTHESIS OF POLYCYCLIC COMPOUNDS RELATED TO THE STEROIDS. XV. STRUCTURE OF THE PRODUCTS OF CONDENSATION OF 2-METHOXYBUTA-1,3-DIENE WITH 1-METHYLCYCLOHEX-1-EN-6-ONE AND METHYL METHACRYLATE

I. N. Nazarov and S. I. Zavyalov

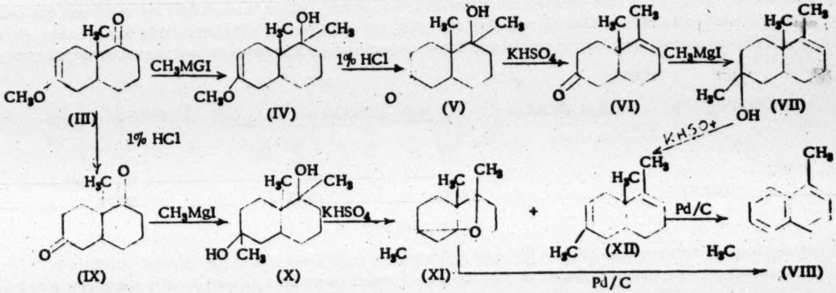
A general method has recently been worked out in our laboratory for the synthesis of polycyclic steroid ketones, with a hydrogenated cyclopentanophenanthrene structure, such as chrysene, cyclopentanofluorene, benzofluorene, and their heterocyclic thia analogs [1]. This synthetic method depended on condensation of bicyclic dienes with α,β-unsaturated cyclic ketones. The basic intermediate product in this synthesis is 6-methoxy-9-methyl-Δ^6-octal-1-one (III), obtained by the condensation of 2-methoxybuta-1,3-diene (I) with 1-methylcyclohex-1-en-6-one (II):


O
CH₃
+
CH₃O
(I)
(II)
O
CH₃
CH₃O
(III)

The structure of the methoxyoctalone derivative (III) was derived from a study of condensations of 2-methoxybuta-1,3-diene with aliphatic α,β-unsaturated aldehydes, ketones, and acids, which in all cases yield p-substituted cyclic products [2]:


CO
+
CH₃O
CO
CH₃O

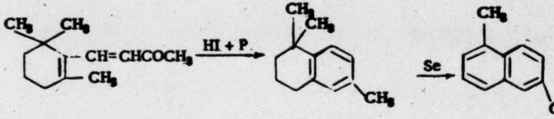
In view, however, of the exceptional importance of the methoxyoctalone (III), it was thought desirable to establish its structure directly, for which purpose we effected the following series of transformations:


H₃C O
CH₃O
(III)
CH₃MGI
H₃C OH CH₃
CH₃O
(IV)
1% HCl
H₃C OH CH₃
O
(V)
KHSO₄
H₃C CH₃
O
(VI)
CH₃MgI
H₃C CH₃
H₃C OH
(VII)
1% HCl
KHSO₄
H₃C O
O
(IX)
CH₃MgI
H₃C OH CH₃
HO CH₃
(X)
KHSO₄
H₃C CH₃
O
H₃C
(XI)
+
H₃C CH₃
H₃C
(XII)
Pd/C
CH₃
H₃C
(VIII)
Pd/C

Magnesium methyl iodide and the methoxyoctalone (III) gave a product which after treatment with dilute hydrochloric acid afforded 1,9-dimethyldecal-1-ol-6-one (V), readily dehydrated by potassium bisulfate to yield 1,9-dimethyl-Δ^1-octal-6-one (VI), and this, by the action of magnesium methyl iodide, affords 1,6,9-trimethyl-Δ^1-octal-6-ol (VII), which when dehydrated and dehydrogenated at a palladium-charcoal catalyst at 330-340° gives 1,6-dimethylnaphthalene (VIII). This was also prepared through the earlier described 1,6-diketo-9-methyldecalin

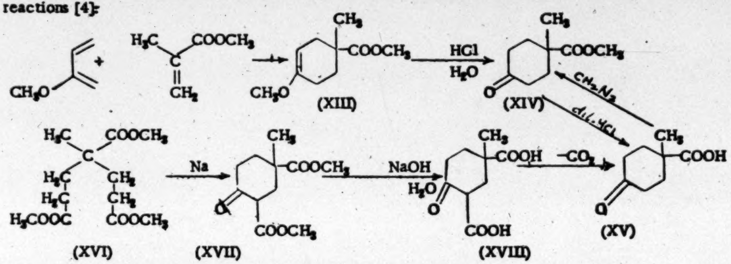
(IX), produced by the hydrolysis of the methoxyoctalone (III) with dilute hydrochloric acid. 1,6-Diketo-9-methyldecalin (IX) by a Grignard reaction with magnesium methyl iodide gives high yields of 1,6-dihydroxy-1,6,9-trimethyldecalin (X), dehydration of which with potassium bisulfate affords a mixture of the hydrocarbon (XII) and the oxide (XI), giving 1,6-dimethylnaphthalene (VIII) when dehydrogenated at a palladized charcoal catalyst.

In order to identify 1,6-dimethylnaphthalene it was synthesized from β-ionone by the following reactions [3]:



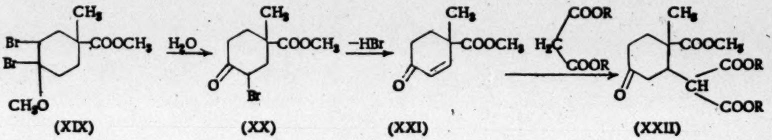
The product so obtained was in every way identical with that given by the methoxyoctalone (III); a mixture of their picrates showed no depression of m.p.

As we expected, methyl methacrylate condenses with 2-methoxybuta-1,3-diene, giving the para-isomer (XIII), the structure of which was established by converting it into the keto-acid (XV) and its methyl ester (XIV), and comparing these products with those obtained from 1,3,5-tricarbomethoxy-3-methyl-n-pentane by known reactions [4]:



The keto-acid (XV) and its ester (XIV) had identical properties; and the mixed m.p. of their semicarbazones and 2,4-dinitrophenylhydrazones showed no depression.

The methoxy-ester (XIII) may be of interest as a starting point for the synthesis of ketones of the hydrindane and decalin series with angular methyl groups. Bromination of the methoxy-ester (XIII) gives the dibromide (XIX), hydrolysis of which yields the bromo-keto-ester (XX), and hydrogen bromide is eliminated from this with production of the unsaturated keto-ester (XXI), addition to which of malonic ester affords the triester (XXII):



EXPERIMENTAL

6-Methoxy-9-methyl-Δ^6-octal-1-one (III), b.p. 88-89°/0.1 mm; n_D^{20} 1.5089), was prepared by condensation of 2-methoxybuta-1,3-diene (I) with 1-methylcyclohex-1-en-6-one (II), as described before [1]. 1,6-Diketo-9-methyldecalin (IX), m.p. 63-65°, was prepared by hydrolysis of the methoxyoctalone (III) [1].

Action of magnesium methyl iodide on 6-methoxy-9-methyl-Δ^6-octal-1-one (III)

A solution of 10 g of 6-methoxy-9-methyl-Δ^6-octal-1-one (III) in 50 ml of absolute ether is added drop by drop, with constant stirring, and cooling in ice, to a Grignard reagent prepared from 1.8 g of magnesium and 13 g of methyl iodide in 50 ml of absolute ether, and the mixture is stirred at room temperature for a further 3 hrs, after which 50 ml of 5% hydrochloric acid is added. The ether layer is separated, the aqueous layer is extracted with ether, the solvent is distilled off from the combined ethereal solutions, and the residue is shaken for 3 hrs. with 20 ml of 1% hydrochloric acid. The product is extracted with ether, the extract is dried with anhydrous sodium sulfate, ether is distilled off, and the residue is vacuum distilled, giving 4.8 g of 6-keto-1-hydroxy-1,9-dimethyldecalin (V), b.p. 118-120°/0.05 mm; n_D^{20} 1.5140.

Found %: C 74.1; H 10.2
$C_{12}H_{20}O_2$. Calculated %: C 73.5; H 10.2

Some of the product undergoes dehydration during the distillation, to afford the unsaturated ketone (VI).

Dehydration of 6-keto-1-hydroxy-1,9-dimethyldecalin (V)

3.5 g of the above product (V) is heated for about 1 hr. at 160-165°/100 mm with 1.8 g of powdered potassium bisulfate, until water ceases to distil over, when the pressure is reduced to 4 mm, at which the dehydration product is distilled over, giving 2.1 g of 6-keto-1,9-dimethyl-Δ^1-octalin (VI), b.p. 104-108°/4 mm; n_D^{20} 1.5099.

Found %: C 81.14; 81.34; H 9.84; 9.97
$C_{12}H_{18}O$. Calculated %: C 80.99; H 10.11

The semicarbazone, m.p. 172-174°, was recrystallized from methanol.

Found %: N 17.69; 17.77
$C_{13}H_{21}ON_3$. Calculated %: N 17.8

Action of magnesium methyl iodide on 6-keto-1,9-dimethyl-Δ^1-octalin (VI)

A solution of 3 g of 6-keto-1,9-dimethyl-Δ^1-octalin (VI) in 10 ml of absolute ether was added drop by drop, with constant stirring, and cooling in ice, to a Grignard solution prepared from 0.6 g of magnesium and 5 g of methyl iodide in 40 ml of absolute ether. The mixture is left for 2 hrs at room temperature, and 20 ml of 1% hydrochloric acid is added, cooling in ice. The product is extracted with ether, and the extract is dried with anhydrous magnesium sulfate, the ether is distilled off, and the residue is fractionally distilled in vacuum, giving 2.6 g of 6-hydroxy-1,6,9-trimethyl-Δ^1-octalin (VII), b.p. 100-105°/3 mm; n_D^{20} 1.5104.

Found %: C 80.18; 80.15; H 11.12; 11.25
$C_{13}H_{22}O$. Calculated %: C 80.41; H 11.34

Dehydration of 6-hydroxy-1,6,9-trimethyl-Δ^1-octalin (VII)

A mixture of 2.9 g of 6-hydroxy-1,6,9-trimethyl-Δ^1-octalin (VII) and 1.5 g of powdered potassium bisulfate was heated for 1 hr at 165-175°, and the resulting hydrocarbon was then distilled over in vacuum. After redistillation at the ordinary pressure, from metallic sodium, 1.4 g of 1,6,9-trimethyl-$\Delta^{1,6}$-hexalin (XII), b.p. 229-231°; n_D^{20} 1.5035.

Found %: C 87.53; 87.41; H 11.47; 11.61
$C_{13}H_{20}$. Calculated %: C 88.57; H 11.43

Dehydrogenation of 1,6,9-trimethyl-$\Delta^{1,6}$-hexalin (XII)

1 g of the hydrocarbon (XII) was vaporized, and the vapor was passed during 2 hrs through a glass tube filled with palladized charcoal (tube length 40 cm, diameter 0.5 cm; 5% Pd in catalyst,) at 330-340°, regulating the rate of flow of the vapor according to the rate of evolution of hydrogen. Fractional distillation of the distillate gave a hydrocarbon of b.p. 130-133°/13 mm; n_D^{20} 1.6078, the picrate of which melted at 108-110° (recrystallized from methanol), and did not depress the m.p. of the picrate of a known specimen of 1,6-dimethylnaphthalene [3].

Action of magnesium methyl iodide on 1,6-diketo-9-methyldecalin (IX)

A solution of 3 g of 1,6-diketo-9-methyldecalin (IX) in 30 ml of absolute ether is added drop by drop, with constant stirring, and cooling in ice, to Grignard reagent prepared from 1.2 g of magnesium and 7.5 g of methyl iodide in 20 ml of absolute ether, after which the mixture is boiled for 3 hrs under reflux, and 20 ml of 1% hydrochloric acid is added to the solution of 0°. The solution is extracted with ether, the ethereal extract is dried with magnesium sulfate, the solvent is distilled off, and the residue is vacuum distilled, giving 3.2 g of 1,6-dihydroxy-1,6,9-trimethyldecalin (X), b.p. 113-116°/0.05 mm; n_D^{20} 1.5115.

Found %: C 73.34; 73.32; H 11.01; 10.97
$C_{13}H_{24}O_2$. Calculated %: C 73.59; H 11.32

Dehydration of 1,6-dihydroxy-1,6,9-trimethyldecalin (X) and dehydrogenation of mixtures of hydrocarbon (XII) and oxide (XI)

A mixture of 4 g of 1,6-dihydroxy-1,6,9-trimethyldecalin (X) and 2 g of potassium bisulfate powder was heated at 150-155°/100 mm, until evolution of water ceased (1 hr). The residue was extracted with ether, and the extract was dried, and distilled from sodium, giving 2.8 g of colorless liquid, b.p. 110-112°/19 mm; n_D^{20} 1.4977.

Found %: C 83.75; 83.59; H 11.41; 11.43
$C_{13}H_{20}$. Calculated %: C 88.57; H 11.43
$C_{13}H_{22}O$. Calculated %: C 80.35; H 11.41

The product appears to be a mixture of 1,6,9-trimethyl-$\Delta^{1,6}$-hexalin (XII) with the corresponding oxide (XI).

Dehydrogenation of 3 g of the mixture under the conditions described above gave 0.7 g of 1,6-dimethylnaphthalene, b.p. 126-128°/10 mm; n_D^{20} 1.6078, picrate, m.p. 108-110° (from methanol), not depressing the m.p. of the picrate of a known specimen of 1,6-dimethylnaphthalene, prepared by a published method from β-ionone, and having m.p. 128-130° at 12 mm; n_D^{20} 1.6083, m.p. of picrate 107-109° [3].

Condensation of 2-methoxybuta-1,3-diene with methyl methacrylate

A mixture of 4 g of 2-methoxybuta-1,3-diene (b.p. 74-75°; n_D^{20} 1.4438), 4.8 g of methyl methacrylate (b.p. 99-100°; n_D^{20} 1.4150), and 0.1 g of pyrogallol in 9 g of dry benzene was heated at 219-220° in a metal tube for 3 hrs, the solvent was distilled off, and the residue was vacuum distilled, giving 5.2 g of 1-carbomethoxy-4-methoxy-1-methylcyclohex-3-ene (XIII), b.p. 107-108°/12 mm; n_D^{20} 1.4722

Found %: C 65.04; 65.32; H 8.98; 8.76
$C_{10}H_{16}O_3$. Calculated %: C 65.22; H 8.69

Preparation of 1-carbomethoxy-4-keto-1-methylcyclohexane (XIV)

5 g of 1-carbomethoxy-4-methoxy-1-methylcyclohex-3-ene (XIII) was shaken with 25 ml of 1% hydrochloric acid for 4 hrs at room temperature, the product was extracted with ether, the extract was dried with sodium sulfate, and distilled in vacuum, giving 3 g of 1-carbomethoxy-1-methylcyclohexan-4-one (XIV), b.p. 99-101°/7 mm; n_D^{20} 1.4610

Found %: C 63.63; 63.92; H 8.69; 8.35
$C_9H_{14}O_3$. Calculated %: C 63.53; H 8.23

The semicarbazone melts at 166-168°, after recrystallization from methanol, and gives no depression with the semicarbazone of a known specimen of the ester [4]; similar results are obtained with the 2,4-dinitrophenylhydrazone, m.p. 125-127° (from benzene), which gives no depression with a known specimen [4].

Preparation of 1-methylcyclohexan-4-one-1-carboxylic acid (XV)

A mixture of 2 g of 1-carbomethoxy-1-methylcyclohexan-4-one (XIV) 6 ml of glacial acetic acid, 1.5 ml of concentrated hydrochloric acid, and 0.9 ml of water was boiled for 6 hrs, volatile products were distilled off, and the residue was distilled in vacuum giving 1-methylcyclohexan-4-one-1-carboxylic acid (XV), b.p. 145-148°/2 mm; m.p. 77-78° (from benzene).

Found %: C 61.32; 61.19; H 7.78; 7.73
$C_8H_{12}O_3$. Calculated %: C 61.54; H 7.69

The m.p. of a known specimen of the acid was not depressed by admixture with our product [4].

1,3-Dicarbomethoxy-1-methylcyclohexan-4-one (XVII)

This ester, b.p. 130-132°/3 mm, n_D^{20} 1.4859), was prepared by the standard method of cyclization of 1,3,5-tricarbomethoxy-3-methyl-n-pentane (XVI) [4].

Hydrolysis of 1,3-dicarbomethoxy-1-methylcyclohexane-4-one (XVII)

5 g of the ester (XVII) was shaken with 40 ml of 5% caustic soda until it dissolved (2-3 min), and the solution was made acid after 8 hrs at room temperature, with dilute (1:1) hydrochloric acid, when 3.7 g of

1-methylcyclohexan-4-one-1:3-dicarboxylic acid (XVIII), m.p. 104-106° (decomp.) separates out.

Found: Equiv. titration 99.3.
$C_9H_{12}O_5$. Calculated: Equiv. titration 100.0.

Decarboxylation of 1-methylcyclohexan-4-one-1,3-dicarboxylic acid (XVIII)

3.7 g of the acid (XVIII) was heated for 1 hour at 120°, until evolution of carbon dioxide ceased, and the residue was recyrstallized from petroleum ether, giving 2.3 g of 1-methylcyclohexan-4-one-1-carboxylic acid (XV), m.p. 76-78°, not depressing the m.p. of a specimen of this acid prepared by diene condensation with the ester (XIII).

Esterification of 1-methylcyclohexan-4-one-1-carboxylic acid (XV)

5 g of the acid (XV) is added gradually, with stirring, to 250 ml of an ethereal solution of diazomethane, prepared from 25 g of nitrosomethylurea, the ether is distilled off, and the residue is distilled in vacuum, giving 4.2 g of 1-carbomethoxy-1-methylcyclohexan-4-one (XIV), b.p. 115-117°/14 mm., n_D^{20} 1,4612 [4].

The semicarbazone, m.p. 168-169°, and the 2:4-dinitrophenylhydrazone, m.p. 127-128°, did not depress the m.p. of the corresponding derivatives of the keto-ester (XIV) prepared by diene condensation of the ester (XIII).

Preparation of 1-carbomethoxy-1-methylcyclohex-2-en-4-one (XXI)

A solution of 8.4 g of dry bromine in 20 g of carbon tetrachloride was added drop by drop, with constant stirring and cooling in ice, to 10 g of 1-carbomethoxy-4-methoxy-1-methylcyclohex-3-ene (XIII) in 30 g of carbon tetrachloride. The solution was then shaken for 15 min. with 62 ml of water, and the lower layer was separated, dried with sodium sulfate, and evaporated down in vacuum. The bromo-ester (XX) so obtained was heated for 1 hour at 150-155° with 9.5 g of dry diethylaniline, and the crystalline product obtained on cooling was treated with dilute (1:1) hydrochloric acid. The product was extracted with benzene, the extract was dried with sodium sulfate, and distilled in vacuum, giving 4 g of 1-carbomethoxy-1-methylcyclohex-2-en-4-one (XXI), b.p. 107-110°/7mm, n_D^{20} 1.4775 [4]. The semicarbazone melted at 157-158°, after recrystallization from methanol.

Found %: N 18.8; 18.6
$C_{10}H_{15}O_3N_3$. Calculated %: N 18.7

Condensation of 1-carbomethoxy-1-methylcyclohex-2-en-4-one (XXI) with malonic ester

4 g of 1-carbomethoxy-1-methylcyclohex-2-en-4-one (XXI) is added during 10 min., with stirring, to a solution of sodio-malonic ester prepared from 15 g of malonic ester and 0.54 of sodium, and the mixture is heated at 70-76° for 7 hours. The cooled solution is made acid at 0° with dilute (1:1) hydrochloric acid, the product is extracted with benzene, the extract is dried with sodium sulfate, and distilled in vacuum, giving 2.2 g of the tricarboxylic ester (XXII), b.p. 155-157°/1.5 mm, n_D^{20} 1.4888.

Found %: C 58.77; 58.91; H 6.62; 6.75
$C_{16}H_{24}O_7$. Calculated %: C 58.60; H 7.30

SUMMARY

Condensation of 2-methoxybuta-1,3-diene with 1-methylcyclohex-1-en-6-one and methyl methacrylate gives the p-substituted products (III) and (XIII), the structure of which was established by converting them into the known compounds (VIII) and (XV), which were also synthesized by standard methods, for their identification.

LITERATURE CITED

[1] I.N. Nazarov, L.D. Bergelson, L.I. Shmonina, and L.N. Terekhova, Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci., No. 4, 439 (1949); I.N. Nazarov et al., J. Gen. Chem., 20, 648, 661, 876 (1950). *

[2] I.N. Nazarov, G.P. Verkholetova, and L.D. Bergelson, Bull. Acad. Sci. U.S.S.R. Div. Chem. Sci. No. 5, 511 (1948); I.N. Nazarov and M.V. Kuvarzina, Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci., No. 6, 599 (1948). A.A. Petrov, J. Gen. Chem., 11, 661 (1941); 17, 538, 1295 (1947); H. Fiesselmann, Ber., 75, 881 (1942).

[3] G. Clemo, Soc. 737 (1935).

[4] M. Rubin, H. Wishinsky, J. Am. Chem. Soc., 68, 338 (1946).

Received January 28, 1952

Institute of Organic Chemistry
Academy of Sciences, U.S.S.R.

---

* See Consultants Bureau English translation, pages 685, 697, 911.

BLANK
PAGE

NEW DATA ON THE CHEMISTRY OF AMIDES OF SULFURIC ACID AND TRICHLOROPHOSPHAZOSULFONARYLS*

A. V. Kirsanov

I. Mechanism of Amidation of Carboxylic Acids with Amides of Sulfuric Acid.

It is known that carboxylic acids react with sulfamides to give amides in almost quantitative yield [1], by the reaction:

$$RCOOH + NH_2SO_2NH_2 \rightarrow RCONH_2 + NH_2SO_2OH.$$

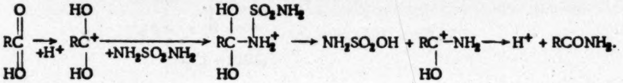
With asymmetrical dimethylsulfamides only dimethylamides are obtained, by the reaction [2]:

$$RCOOH + (CH_3)_2NSO_2NH_2 \rightarrow RCON(CH_3)_2 + NH_2SO_2OH.$$

Symmetrical diphenylsulfamides give anilides of the appropriate acids, by the reaction:

$$RCOOH + C_6H_5NHSO_2NHC_6H_5 \rightarrow RCONHC_6H_5 + C_6H_5NHSO_2OH.$$

These reactions may be explained by a mechanism analogous to that of esterification [1], i.e.:



$$\underset{\text{HO}}{\overset{\text{O}}{\text{RC}}}\xrightarrow[+H^+]{}\underset{\text{HO}}{\overset{\text{HO}}{\text{RC}^+}}\xrightarrow[+NH_2SO_2NH_2]{}\underset{\text{HO}}{\overset{\text{HO}}{\text{RC}}}-\overset{SO_2NH_2}{NH_2^+}\longrightarrow NH_2SO_2OH+\underset{\text{HO}}{\text{RC}^+}-NH_2\longrightarrow H^+ + RCONH_2.$$

If this mechanism is in fact applicable, it must follow that any sulfamide should be capable of amidating carboxylix acids, including tri- and tetra-substituted sulfamides; the presence of a "free" hydrogen atom in the sulfamide molecule is not essential.

An experimental study of the reaction of amidation of carboxylic acids (acetic and benzoic) with tetrasubstituted sulfamides (tetramethyl- and symmetrical diphenyldimethyl- and diphenyldiethyl-sulfamide) showed that the reaction:

$$(CH_3)_2NSO_2N(CH_3)_2 + RCOOH \not\longrightarrow RCON(CH_3)_2 + (CH_3)_2NSO_2OH,$$

does not take place, the sulfamides being recovered unreacted in amounts of 99.1 – 99.4%, and the benzoic acid in amounts of 97.8 – 98.5%, in a pure state. It follows that the proposed mechanism cannot be the correct one.

It is evident that the presence within the sulfamide molecule of "free" hydrogen atoms is essential for the amidation reaction, and that such "free" atoms (or atom) must enter into the reaction mechanism. In order to ascertain whether there must be one or two "free" hydrogen atoms in the sulfamide molecule a study was made of the reaction between tri-substituted sulfamides and carboxylic acids (trimethylsulfamide and asymmetrical phenyldimethylsulfamide with benzoic and p-nitrobenzoic acid). The reaction proceeded smoothly; only the dimethylamide of the carboxylic acid was obtained with trimethylsulfamide, as follows:

$$RCOOH + (CH_3)_2NSO_2NHCH_3 \rightarrow RCON(CH_3)_2 + CH_3NSO_2OH.$$

With phenyldimethylsulfamide the products are dimethylamide and anilide, by the reaction:

$$RCOOH + (CH_3)_2NSO_2NHC_6H_5 \rightarrow \underset{\sim 55\%}{RCON(CH_3)_2} \text{ and } \underset{\sim 30\%}{RCONHC_6H_5}$$

---

* Read at a general meeting of the Division of Chemical Sciences of the Academy of Sciences, U.S.S.R. on March 27, 1952.

It follows that it is sufficient for the reaction of amidation that the sulfamide should contain at least one "free" hydrogen atom, i.e., all except tetra-substituted sulfamides can be used for amidation.

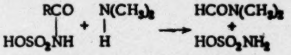
The definite conclusion may be drawn that intermediate products of the reaction must be either acylsulfamides or acylsulfamic acids:

$$RCONHSO_2NH_2; \qquad RCONHSO_2OH.$$

At first sight, however, it then appears inexplicable how dialkylamides can be formed. It seems that hydrolysis of acylsulfamides can give only amides or monoalkylamides. These contradictions appeared for a long time to be irreconcilable, but the explanation was eventually found. Apparently the water formed in the production of acylsulfamide hydrolyzes the "free" amino-group of acylsulfamide, giving the ammonium salt of acylsulfamic acid, as follows:

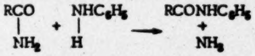
$$RCOOH + NH_2SO_2N(CH_3)_2 \rightarrow RCONHSO_2N(CH_3)_2 + H_2O \rightarrow RCONHSO_2O^- + (CH_3)_2NH_2^+.$$

The action of pyridine on the salt gives free ammonia or amine, which causes aminolysis of the C–N bond, with formation of amide, monosubstituted amide, or disubstituted amide, by the reaction:



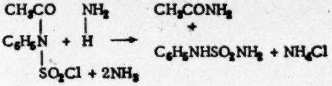
$$\begin{array}{c}RCO\\|\\HOSO_2NH\end{array} + \begin{array}{c}N(CH_3)_2\\|\\H\end{array} \longrightarrow \begin{array}{c}HCON(CH_3)_2\\+\\HOSO_2NH_2\end{array}$$

Analogous cases of aminolysis are known, such as the reaction of trans-amination of carboxylic acids [3]:



$$\begin{array}{c}RCO\\|\\NH_2\end{array} + \begin{array}{c}NHC_6H_5\\|\\H\end{array} \longrightarrow \begin{array}{c}RCONHC_6H_5\\+\\NH_3\end{array}$$

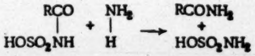
and the aminolysis of chlorides of arylacylsulfamic acids [4]:



$$\begin{array}{l}CH_3CO\\ \quad|\\C_6H_5N\\ \quad|\\ \quad SO_2Cl + 2NH_3\end{array} + \begin{array}{c}NH_2\\|\\H\end{array} \longrightarrow \begin{array}{c}CH_3CONH_2\\+\\C_6H_5NHSO_2NH_2 + NH_4Cl\end{array}$$

It is thus quite likely that acylsulfamic acids are in fact intermediate products of the reaction of amidation, which would thus proceed as follows:

$$RCOOH + NH_2SO_2NH_2 \rightarrow RCONHSO_2ONH_4;$$

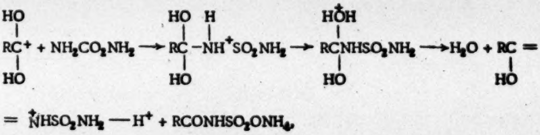


$$\begin{array}{c}RCO\\|\\HOSO_2NH\end{array} + \begin{array}{c}NH_2\\|\\H\end{array} \longrightarrow \begin{array}{c}RCONH_2\\+\\HOSO_2NH_2\end{array}$$

Acylsulfamic acids may be formed in two ways; either isosulfanic acid is formed as an intermediate product, i.e., the reaction proceeds as follows:

$$(CH_3)_2NSO_2NHC_6H_5 \rightarrow C_6H_5N = SO_2 \xrightarrow[+RCOOH]{} RCON(C_6H_5)SO_2OH$$

or, as is more probable, the reaction mechanism is analogous to that of esterification, but differs in certain respects from that previously proposed:

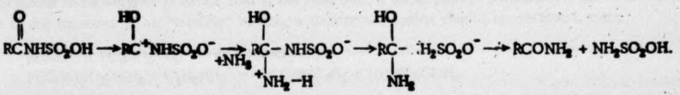


$$\begin{array}{c}HO\\|\\RC^+\\|\\HO\end{array} + NH_2CO_2NH_2 \rightarrow \begin{array}{l}HO\;\;H\\ \,|\quad\;|\\RC-NH^+SO_2NH_2\\ \,|\\HO\end{array} \rightarrow \begin{array}{l}H\overset{+}{O}H\\ \;|\\RCNHSO_2NH_2\\ \;|\\HO\end{array} \rightarrow H_2O + \begin{array}{c}RC =\\|\\HO\end{array}$$

$$= \overset{+}{N}HSO_2NH_2 - H^+ + RCONHSO_2ONH_4,$$

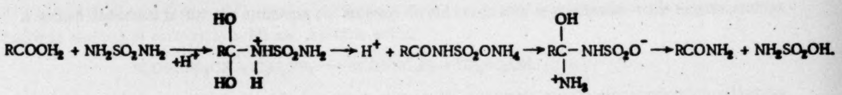
i.e., the product of addition of sulfamide to the active complex of the acid eliminates water, and not sulfamic acid, in the same way as in the reaction of esterification. This reaction scheme is thus far closer to that of esterification than was the original, incorrect scheme.

It is quite possible that pyridine takes part in the amidation reaction, which either does not proceed at all in its absence, or does so only at higher temperatures, giving low yields. Numerous attempts have been made to isolate intermediate products containing pyridine, without any success; these products are evidently highly unstable, and enter into further reaction as soon as they are formed. It is probable that the product of addition of pyridine to sulfamide is formed first, possibly being of the type of a betainopyridonium salt of sulfamic acid, and the sulfamide so activated then reacts with the carboxylic acid according to the above scheme; formation of imidosulfamide in the reaction of pyridine with sulfamide has been thus explained [5], and aminolysis may take place in the same way, i.e.:



$$\overset{O}{\overset{\|}{RC}}NHSO_2OH \rightarrow R\overset{HO}{\overset{|}{C}}{}^{+}NHSO_2O^- \xrightarrow[+NH_3]{} R\underset{{}^{+}NH_2-H}{\underset{|}{\overset{HO}{\overset{|}{C}}}}-NHSO_2O^- \rightarrow R\underset{NH_2}{\underset{|}{\overset{HO}{\overset{|}{C}}}}-NH_2SO_2O^- \rightarrow RCONH_2 + NH_2SO_2OH.$$

It is thus very probable that the reaction of amidation of carboxylic acids by sulfamides proceeds according to the following mechanism:



$$RCOOH_2 + NH_2SO_2NH_2 \xrightarrow[+H^+]{} R\underset{HO}{\underset{|}{\overset{HO}{\overset{|}{C}}}}-\underset{H}{\underset{|}{\overset{+}{N}}}HSO_2NH_2 \rightarrow H^+ + RCONHSO_2ONH_4 \rightarrow R\underset{{}^{+}NH_3}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-NHSO_2O^- \rightarrow RCONH_2 + NH_2SO_2OH.$$

This reaction mechanism explains all the observed facts except one. If it is the correct mechanism, we should expect to obtain only dimethylamides from phenyldimethylsulfamide and carboxylic acids, by the scheme:

$$RCOOH + (CH_3)_2\,NSO_2NHC_6H_5 \rightarrow RCON(C_6H_5)SO_2OH + NH(CH_3)_2 \rightarrow RCON(CH_3)_2 + C_6H_5NHSO_2OH,$$

whereas in fact we obtain a mixture of dimethylamides and anilides. This may mean that the proposed mechanism is not the actual one, or that some other, additional factors enter into the picture. Examination of the above scheme shows that it differs basically from the general one for unsubstituted sulfamides. In the reaction between carboxylic acids and unsubstituted or asymmetrically disubstituted sulfamides stable, difficulty hydrolyzable sulfamic acid is obtained as a by-product, whereas with phenyldimethylsulfamide the by-product is unstable, very readily hydrolyzable phenylsulfamic acid. This acid gives stable salts, but it is so unstable in the free state that it has never yet been isolated. Two authors who claim to have done so give melting points of 77° [6] and over 280° [7]. The acid tends to undergo hydrolysis at the nitrogen-sulfur bond, so that there is strong reason to believe that carboxylic acids should cause acidolysis of phenylsulfamic acid, as follows:

$$C_6H_5NHSO_2OH + RCOOH \rightarrow RCONHC_6H_5 + HOSO_2OH,$$

i.e., with formation of anilides. This supposition was confirmed by experiment.

Ammonium phenylsulfamate was prepared from sulfamic acid and aniline by the reaction:

$$C_6H_5NH_2 + NH_2SO_2OH \rightarrow C_6H_5NHSO_2ONH_4$$

and was heated, without prior purification, with p-nitrobenzoic acid in pyridine solution, giving the corresponding anilide in ~30% yield; this confirms the accuracy of our theoretical supposition, and also gives us a new method for the direct conversion of carboxylic acids into their anilides. It is possible that this method may be adopted in practice, since arylsulfamic acids are readily available as their ammonium salts.

Formation of anilides from phenylsulfamic acid and carboxylic acids was also confirmed by another experiment, in which 2 g-mols. of p-nitrobenzoic acid in pyridine was heated with 1 g-mol. of phenylsulfamide, giving p-nitrobenzanilide in 73.6% yield, by the reaction:

$$2RCOOH + C_6H_5NHSO_2NHC_6H_5 \rightarrow 2RCONHC_6H_5 + H_2SO_4,$$

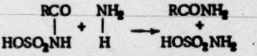
or in 147.2% yield by the reaction:

$$RCOOH + C_6H_5NHSO_2NHC_6H_5 \rightarrow RCONHC_6H_5 + C_6H_5NHSO_2OH.$$

This can only be explained on the assumption that the carboxylic acid acidolyzes phenylsulfamic acid, giving phenylsulfamide. Unsubstituted sulfamic acid and alkylsulfamic acids do not under such conditions react with carboxylic acids.

The reaction mechanism presented by us for the reaction of amidation is thus in conformity with all the observed facts. However, a theory should not only explain all the known facts; it should also predict as yet unknown ones. Let us see what our theory predicts, and how the predictions are confirmed by experiment.

The second stage of the reaction consists of aminolysis of acylsulfamic acid:



$$\begin{matrix} RCO \\ | \\ HOSO_2NH \end{matrix} + \begin{matrix} NH_2 \\ | \\ H \end{matrix} \longrightarrow \begin{matrix} RCONH_2 \\ + \\ HOSO_2NH_2 \end{matrix}$$

The first conclusion to be derived is hence that if the reaction of amidation is performed with an unsubstituted sulfamide, but in the presence of an "outside" amine, a substituted amide should be obtained, e.g.:

$$RCOOH + NH_2SO_2NH_2 \longrightarrow RCONHSO_2ONH_4$$
$$RCONHSO_2ONH_4 + C_6H_5NH_2 \longrightarrow RCONHC_6H_5 + NH_2SO_2ONH_4.$$

This was confirmed for the case sulfamide – p-nitrobenzoic acid – aniline. The yields, calculated on reacted p-nitrobenzoic acid, were: anilide ~58%, unsubstituted amide ~36% of theory.

A second deduction is that the ammonia (or amides) should react with acylsulfamic acids to give amides (or substituted amides) of carboxylic acids and sulfamic acids:

$$RCONHSO_2OH + C_6H_5NH_2 \longrightarrow RCONHC_6H_5 + NH_2SO_2OH.$$

Pyridonium benzoylsulfamate was prepared by heating a mixture of benzamide and betainopyridonium sulfamate, and the reaction product (without separating benzoylsulfamate) was heated with aniline, giving ~70% yield of benzanilide, calculated on reacted benzamide. Our second deduction is thus confirmed.

Acylsulfamic acids have up to now been little studied, but there is reason to believe that they may become cheap and readily available substances, in which case this reaction may become of commercial interest.

A third deduction is that polypeptides should be obtained by the action of sulfamides on amino-acids. Thus p-aminobenzoylsulfamic acid should be obtained as an intermediate product in the reaction between sulfamide and p-aminobenzoic acid:

$$NH_2C_6H_4COOH + NH_2SO_2NH_2 \longrightarrow NH_2C_6H_4CONHSO_2OH + NH_3.$$

This product may then undergo aminolysis at the carbon-nitrogen bond when treated with ammonia, to give p-aminobenzamide, or, by reaction with the amino-group of p-aminobenzoic acid, it may give the dipeptide of aminobenzoic acid, as follows:

$$NH_2C_6H_4CONHSO_2OH + NH_3 \longrightarrow NH_2C_6H_4CONH_2 + NH_2SO_2OH;$$
$$NH_2C_6H_4CONHSO_2OH + NH_2C_6H_4COOH \longrightarrow NH_2C_6H_4CONHC_6H_4COOH + NH_2SO_2OH.$$

Of these two, the second reaction should be the faster one, since the amino-group is, at least initially, present in greater concentration than the ammonia, especially if free ammonia enters into the reaction, having been displaced from the salt by pyridine. But if dipeptide is formed there is no reason to suppose that the same process will not go further, to give tripeptide, tetrapeptide, and so on.

$$nNH_2C_6H_4COOH + nNH_2SO_2NH_2 \longrightarrow NH_2C_6H_4CO(NHC_6H_4CO)_{n-2}NHC_6H_4CONH_2 + (n + 1)NH_2SO_2ONH_4 + NH_2SO_2OH.$$

Only experiment can show which will be the final product formed by this process. The degree of condensation will obviously depend on the solubility of the polypeptides in the reaction medium and on the experimental conditions in general.

All these theoretical conclusions emerging from our proposed reaction mechanism were confirmed experimentally. The action of sulfamide on p-aminobenzoic acid in pyridine solution, at temperatures not greater than 100°, i.e., under the ordinary amidation conditions, gives a mixture of polypeptides of p-aminobenzoic acid, in good yield. The main product is a colorless, infusible mass of polypeptides, insoluble in the usual organic solvents. As was to be expected, no p-amino-benzamide was obtained. Amidation and phenylamidation of p-dimethylaminobenzoic acid, however, gave good yields of p-dimethylaminobenzamide- or -benzanilide, as would follow from our theory.

It would have been of very great interest to prepare polypeptides in the same way from aliphatic amino-acids, but this could not be realized, because of the insolubility in pyridine of the simpler amino-acids, such as alanine or glycine, which cannot thus be made to react with sulfamides.

The reaction mechanism proposed by us for amidation of carboxylic acids with sulfamides not only gives a satisfactory explanation of all the known reactions, but has led to the finding of further applications of this reaction, such as the finding of a new variant, that of preparation of anilides by reaction with phenylsulfamic acid. Our mechanism also allowed us to predict the effect of adding another amine to the reaction systems, to predict that acylsulfamic acids should give amides with amines, and that amino-acids soluble in pyridine should give polypeptides instead of amides in the conditions of the reaction.

II. New Method of Preparation of Trichlorophosphazosulfonaryls

Trichlorophosphazosulfonaryls are, as is known, prepared by the action of phosphorus pentachloride on sulfonamides [9]. This method is very convenient for the trichloro-derivatives, and it might conceivably be extended to tribromophosphazosulfonaryls, but it certainly could not be applied to preparation of triiodophosphazosulfonaryls or of arsazosulfonaryls.

The limitations of this method led us to seek for a new method of a more general nature, applicable to preparation of analogs of trichlorophosphazosulfonaryl I : in which both the halogen and the phosphorus are replaced by other elements. Such a method was recently found; it depends on the action of alkali metal salts of sulfochloramides : on phosphorus trichloride, by the reaction:

$$ArSO_2NNaCl + PCl_3 \longrightarrow NaCl + ArSO_2N = PCl_3.$$

which proceeds smoothly, giving practically quantitative yields. Substitution of phosphorus tribromide for trichloride gives the corresponding tribromo-derivative, and of arsenious for phosphorus trichloride the corresponding arsenic compound.

III. Hydrolysis and Aminolysis of Trichlorophosphazosulfonaryl*

Hydrolysis of trichlorophosphazosulfonaryls I. should proceed as follows:

$$ArSO_2N = PCl_3 \xrightarrow[+H_2O]{} ArSO_2NHPOCl_2 \xrightarrow[+H_2O]{} ArSO_2NHPO(OH)Cl \xrightarrow[+H_2O]{} ArSO_2NHPO(OH)_2 \xrightarrow[+H_2O]{}$$

$$\longrightarrow ArSO_2NH_2 + H_3PO_4.$$

Hydrolysis was studied in solutions in acetone, ethers, and esters, and in all cases very difficultly separable mixtures were obtained, from which only very small yields of crystalline hydrolysis products were isolated. Satisfactory results were obtained by hydrolysis with steam in benzene solution, whereby were obtained the dichlorides of phenyl-, o-tolyl-, p-tolyl-, and 1-naphthyl-sulfonamidophosphoric acid in good yield.

Since all attempts at obtaining products in which the second and third halogen atoms have undergone hydrolysis were unsuccessful, we decided to apply acidolysis instead of hydrolysis, in the expectation that this would give the same products as would have hydrolysis, with the difference that the by-product would be the acid chloride instead of hydrogen chloride, as follows:

$$ArSO_2N = PCl_3 + CH_3COOH \longrightarrow ArSO_2NHPOCl_2 + CH_3COCl.$$

Apart from this the final product of acidolysis should be acylsulfamide instead of sulfamide, such as:

$$C_6H_5SO_2NHPO(OH)_2 + CH_3COOH \longrightarrow C_6H_5SO_2NHCOCH_3 + H_3PO_4.$$

Experiments performed with acetic and benzoic acids showed, however, that it is not possible to use any acid in order to achieve all the intermediate degrees of acidolysis. The acid chlorides formed as byproducts react with trichlorophosphazosulfonaryls when heated, giving cyanides and arylsulfochlorides [10], as follows:

$$ArSO_2H{=\!=}PCl_3 + RCOCl \longrightarrow RCN + ArSO_2Cl + POCl_3.$$

which greatly complicates the isolation in a pure state of acidolysis products.

It was therefore necessary to find an acid which would not give rise to undesirable by-products; formic acid should theoretically be suitable, as its chloride decomposes as soon as it is formed, giving hydrogen chloride and carbon monoxide. This was confirmed experimentally, all stages of hydrolysis being obtained in good yield, viz., arylsulfonamidophosphoric acid, and its mono- and di-chlorides. In general, formic acid may be recommended as an excellent reagent for conversion of acid chlorides into the free acids.

Experiments on acidolysis were performed on five trichlorophosphazosulfonaryls (phenyl, o- and p-tolyl, and 1- and 2-naphthyl), using three acids (formic, acetic and benzoic). With acetic and benzoic acid only products of the first degree of hydrolysis were obtained in good yield. All the intermediate products of hydrolysis of trichlorophosphazosulfonaryls are crystalline substances, fairly readily hydrolyzable, and readily entering into reaction with alcohols, phenols, and aromatic and aliphatic amines. Some of them have an extremely bitter taste. They are all only very slightly toxic.

---

* E. A. Abrazhanova's experiments.

Acidolysis of arylsulfonamidophosphoric acids gives sulfamides, together with acylsulfamides; this is due to thermal decomposition of the acids, as follows:

$$ArSO_2NHPO(OH)_2 \longrightarrow ArSO_2NH_2 + HPO_3.$$

Ammonia reacts with trichlorophosphazosulfonaryls to give triamides of arylsulfonimidophosphoric acids (triaminophosphazosulfonaryls), as follows:

$$ArSO_2N = PCl_3 + 6NH_3 \longrightarrow ArSO_2N = P(NH_2)_3 + 3NH_4Cl.$$

These are crystalline substances, fairly soluble in water.

The triamides of arylsulfonamidophosphoric acids appear to be the first compounds described in which a phosphorus atom is joined to four atoms of nitrogen. Aqueous solutions of triamides have a neutral reaction, and cannot be titrated with phenolphthalein indicator, but the triamides gives mono-silver salts. They are fairly quickly hydrolyzed in aqueous solution, giving ammonium salts of diamidoarylsulfonimidophosphoric acids, as follows:

$$ArSO_2N = P(NH_2)_3 + H_2O \longrightarrow ArSO_2N' = P(NH_2)_2\,(ONH_4).$$

These ammonium salts are converted by the action of silver nitrate solution into the corresponding silver salts, which are colorless, finely crystalline substances, sparingly soluble in water. The free acids could not be obtained, as when the solutions of their salts were made acid hydrolysis of another amino-group took place, giving monoamidoarylsulfonamidophosphoric acid, as follows:

$$ArSO_2N = P(NH_2)_2(ONH_4) \xrightarrow[+2H^+ + H_2O]{} 2NH_4^+ + ArSO_2N = P(NH_2)(OH)_2.$$

When aqueous solutions of triamides (not acidified) are boiled, sulfamides and ammonium diamidophosphate are formed, by the reactions:

$$ArSO_2N = P(NH_2)_3 \xrightarrow[+H_2O]{} ArSO_2N = P(NH_2)_2(ONH_4) \xrightarrow[+H_2O]{} ArSO_2NH_2 + (NH_2)_2PO(ONH_4).$$

Free diamidoarylsulfonamidophosphoric acids thus readily undergo hydrolysis at the phosphotus – amino-group bond, whereas salts of diaminophosphoric acids are hydrolysed at the phosphorus – arylsulfonamido-group bond.

Only the monoamides of arylsulfoamidophosphoric acids were obtained by the action of ammonia on dichlorides of arylsulfonamidophosphoric acids; for this reason the diamides of arylsulfonamidophosphoric acids have not yet been prepared; the monoamides always being obtained. The monoamides of arylsulfonamidophosphoric acids are most conveniently prepared by the action of aqueous ammonia on trichlorophosphazosulfonaryls or on the dichlorides of arylsulfonamidophosphoric acids they are crystalline, acidic substances, titratable as dibasic acids, and readily hydrolyzed in boiling aqueous solution.

Aromatic amines react with trichlorophosphazosulfonaryls as follows:

$$ArSO_2N = PCl_3 \xrightarrow[+4C_6H_5NH_2]{} ArSO_2N = PCl(NHC_6H_5)_2 \xrightarrow[+2C_6H_5NH_2]{} ArSO_2N = P(NHC_6H_5)_3.$$

This reaction was studied in the cases of four different trichlorophosphazosulfonaryls (phenyl, o-tolyl, p-tolyl, and 1-naphthyl) and two amines (aniline and p-toluidine). The products of the first stage of the process, viz., the monochlorides of dianilidoarylsulfonimidophosphoric acids, are crystalline substances, readily hydrolyzable to the corresponding acids. The free dianilidoarylsulfonamidophosphoric acids behave as monobasic acids, and do not undergo hydrolysis in aqueous solutions even when these are heated. They are, however, readily hydrolyzed by boiling with strong mineral acids.

The final products of the reaction, viz., the trianilides of aryl-sulfonimidophosphoric acids, are neutral crystalline substances, insoluble in alkaline solutions, and not hydrolyzed when boiled with water. It is of interest that one of these trianilides has long been known, although its structure was not known; this is the trianilide of the structure:

$$CH_3C_6H_4NHCOC_6H_4SO_2N = P(NHC_6H_4CH_3)_3.$$

obtained by Rodionov and Yavorsky [8] in 1948 by the action of p-toluidine on the chloride of p-trichlorophosphazosulfobenzoic acid.

IV. Reaction of Trichlorophosphazosulfonaryls with Alcohols and Phenols*

As was to be expected, trichlorophosphazosulfonaryls react with alcohols similarly to phosphorus oxychloride, i.e., according to the experimental conditions they form either esters of arylsulfonamidophosphoric acid or alkyl halides and free arylsulfonamidophosphoric acids, or both processes may take place simultaneously. The reaction products should thus be: triesters of arylsulfonimidophosphoric acids, diesters of arylsulfonamidophosphoric acids, monoesters of arylsulfonamidophosphoric acids, and free arylsulfonamidophosphoric acids:

$$ArSO_2N = PCl_3 + 3ROH \longrightarrow ArSO_2N = P(OR)_3 + 3HCl,$$

or

$$ArSO_2N = P(OH)(OR)_2 + RCl + 2HCl,$$

or

$$ArSO_2N = P(OH)_2(OR) + 2RCl + HCl,$$

or

$$ArSO_2N = P(OH)_3 + 3RCl.$$

The triesters are formed together with diesters from trichlorophosphazosulfonaryls and sodium alkoxide or phenoxide in alcoholic solution or in neutral solvents.

The diesters are obtained in almost quantitative yield by the action of sodium alkoxides on dichlorides of arylsulfonamidophosphoric acids, as follows:

$$ArSO_2NHPOCl_2 + 3RONa \longrightarrow ArSO_2N = P(OR)_2(ONa) + 2NaCl + ROH.$$

The tri-methyl, -ethyl, -butyl, -phenyl, and -nitrophenyl esters of 1- and 2-naphthylsulfonimidophosphoric acid are crystalline substances of low melting point. The methyl and ethyl esters are slowly hydrolyzed by boiling aqueous alkalis, giving the diesters. The nitrophenyl esters are very readily hydrolyzed. The tri-methyl, -ethyl, and -butyl esters of phenyl- and o-tolyl-sulfonimidophosphoric acids are odorless low m.p. solids or liquids.

The di-methyl, -ethyl, -butyl, -phenyl, and -nitrophenyl esters of arylsulfonamidophosphoric acids are crystalline, very bitter substances, which can be titrated as monobasic acids with phenolphthalein indicator; they give crystalline salts. The sodium salt of dibutyl esters is soluble in benzene, and can be crystallized from petroleum ether.

SUMMARY

1. A scheme explaining the reactions of amidation of carboxylic acids by amides of sulfuric acid is presented, and is experimentally established.

2. It is shown that phenylsulfamic acid in pyridine solution reacts with carboxylic acids to give their anilides.

3. The product of reaction of amines with acylsulfamic acids is shown to be an acylamine.

4. The products of reaction of p-aminobenzoic acid with sulfamides are shown to be polypeptides of p-aminobenzoic acid.

5. A new method has been found for preparation of trihalogenophosphazosulfonaryls, from alkali metal salts of chloramides of arylsulfonic acids and the appropriate phosphorus trihalides.

6. The hydrolysis and acidolysis of trichlorophosphazosulfonaryls have been studied. All the theoretically possible intermediate and final products of hydrolysis and acidolysis of trichlorophosphazosulfonaryls were obtained, viz., the mono- and di-chlorides of arylsulfonamidophosphoric acids, free arylsulfonamidophosphoric acids, and acylsulfamides.

7. The aminolysis and arylaminolysis of trichlorophosphazosulfonaryls have been studied. The products are: triamides of arylsulfonimidophosphoric acids, salts of diamides of arylsulfonimidophosphoric acids, monoamides of arylsulfonamidophosphoric acids, chlorides of dianilidoarylsulfonimidophosphoric acids, dianilides of

---

* V. I. Shevchenko's experiments.

arylsulfonamidophosphoric acids, and trianilides of arylsulfonimidophosphoric acids.

8. The reaction between trichlorophosphazosulfonaryls and alcohols or phenols has been studied. The products are triesters of arylsulfonimidophosphoric acids and diesters of arylsulfonamidophosphoric acids.

LITERATURE CITED

[1] A. V. Kirsanov and Yu. M. Zolotov, J. Gen. Chem., 19, 2201 (1949). •

[2] A. V. Kirsanov and Yu. M. Zolotov, J. Gen. Chem., 21, 1166 (1951). ••

[3] C Hurd, M. Dull and K. Martin, J. Am. Chem. Soc.,54, 1974 (1932).

[4] M. Battegayet, I. Meybeck, C. r. 194, 186 (1932); I. Meybeck, Ann. Chem. (10), 17, 129 (1932); L. Denivelleet, I. Meybeck, C. r. 193, 1195 (1931).

[5] A. V. Kirsanov and Yu. M Zolotov, J. Gen. Chem., 20, 1650 (1950). •••

[6] Wohl and Koch, Ber. 43, 3297; Ann. 4 (1910).

[7] Buhner, A.,333, 288 (1904).

[8] V. M. Rodionov and E. V. Yavorskaya, J. Gen. Chem., 18, 110 (1948).

[9] A. V. Kirsanov, J Gen. Chem., 22, 269 (1952). ••••

[10] A. V. Kirsanov, J. Gen. Chem., 22, 274 (1952). •••••

Received April 26, 1952

Stalin Dnepropetrovsk Metallurgical Institute

• See Consultants Bureau English Translation, p. a-675.

•• See Consultants Bureau English Translation, p. 1273.

••• See Consultants Bureau English Translation, p. 1713.

•••• See Consultants Bureau English Translation, p. 329.

••••• See Consultants Bureau English Translation, p. 335.

NEW METHOD FOR SYNTHESIS OF PHOSPHINIC AND THIOPHOSPHINIC ACID ESTERS*

PART II. ADDITION OF DIALKYLPHOSPHOROUS ACIDS TO THE AMIDE AND ESTERS OF METHACRYLIC ACID

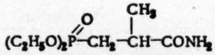
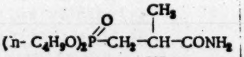
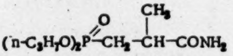
A. N. Pudovik and D. Kh. Yarmukhametova

It has been shown by one of us that a very simple method for the synthesis of phosphonecarboxylic acids is to add dialkylphosphorous acids to esters of unsaturated carboxylic acids. Addition of dimethyl-, diethyl-, dibutyl, and diisobutyl-phosphorous acids to methyl acrylate [1], methyl methacrylate [2], ethyl crotonate, and ethyl cinnamate gave the esters of dialkylphosphone-propionic, -isobutyric, and -phenylpropionic acids, in quantitative yields. In this paper we shall describe the results of attempted addition of dialkylphosphorous acids to amides of unsaturated acids, of higher dialkylphosphorous acids to esters of $\alpha\beta$-unsaturated acids, and of dialkylphosphorous acids to esters of unsaturated carboxylic acids with various alcohols. The experiments were done with the amide and esters of methacrylic acid.

Addition of dialkylphosphorous acids to the amide was effected in the presence of alkali metal alkoxides. The reaction proceeded quite energetically, with evolution of considerable heat, giving the amides of diethyl-, dipropyl-, and di-n-butyl-phosphoneisobutyric acid; the constants of the products, and their yields, are given in Table 1.

It appears from Table 1 that the yields are low, not exceeding 31% (ethyl ester). We were not able to prepare the product of addition of dimethylphosphorous acid to methacrylamide, as it decomposed when distilled. Addition of dihexyl-, diheptyl-, and dioctyl-phosphorous acid to methyl methacrylate was next studied; the reaction proceeds fairly readily, with evolution of heat, but the yields were much lower than with lower mol. wt. dialkylphosphorous acids. The constants of the products obtained are given in Table 2.

TABLE 1

Serial No.	Formula	B.p. °C/p in mm	n_D^{20}	D_4^{20}	Yield %
1	 $(C_2H_5O)_2\overset{O}{\overset{//}{P}}-CH_2-\overset{CH_3}{\overset{\mid}{C}}H-CONH_2$	146-147/13	1.4361	1.0624	31
2	 $(n\text{-}C_4H_9O)_2\overset{O}{\overset{//}{P}}-CH_2-\overset{CH_3}{\overset{\mid}{C}}H-CONH_2$	164-165/12	1.4421	0.9941	15
3	 $(n\text{-}C_3H_7O)_2\overset{O}{\overset{//}{P}}-CH_2-\overset{CH_3}{\overset{\mid}{C}}H-CONH_2$	135°/2	1.4438	1.0437	17

Finally, addition of diethylphosphorous acid to alkyl methacrylates (the alkyl being ethyl to octyl) was studied; the reaction proceeds energetically in most cases. The constants and yields of the products are given in Table 3, from which it appears that the yields are lower than with methyl methacrylate (74.5%).

EXPERIMENTAL

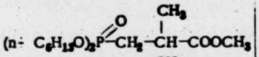
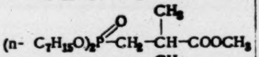
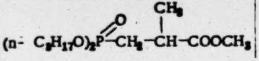
Addition of Diethylphosphorous Acid to Methacrylamide

A concentrated solution of sodium ethoxide in absolute ethanol was added gradually to 8 g of diethylphosphorous acid and 5 g of methacrylamide in an Arbuzov flask. The reaction proceeds energetically, with considerable

---

* This and succeeding papers are parts of a series having the general title "Addition of dialkylphosphorous acids to unsaturated compounds," published in the Journal of General Chemistry during the past two years. The change in the general title is due to the circumstance that the new synthesis of esters of phosphorous acid discovered by us was originally based on addition of dialkylphosphorous acids to unsaturated electronophilic reagents, but has now been extended to certain saturated compounds, and to esters of other types of acids derived from phosphorus.

TABLE 2

Serial No.	Formula	B.p. °C/p in mm	n_D^{20}	d_4^{20}	Yield %
1	 $(n\text{-}\ C_6H_{13}O)_2\overset{O}{\overset{/\!/}{P}}-CH_2-\overset{CH_3}{\overset{\mid}{C}}H-COOCH_3$	188-189/4	1.4442	0.9900	20
2	 $(n\text{-}\ C_7H_{15}O)_2\overset{O}{\overset{/\!/}{P}}-CH_2-\overset{CH_3}{\overset{\mid}{C}}H-COOCH_3$	183-185/1	1.4480	0.9653	14
3	 $(n\text{-}\ C_8H_{17}O)_2\overset{O}{\overset{/\!/}{P}}-CH_2-\overset{CH_3}{\overset{\mid}{C}}H-COOCH_3$	193-194/1	1.4489	0.9461	16

evolution of heat after the addition of each drop, initially. Further addition of ethoxide is discontinued when heat is no longer evolved (usually after the 8 - 10th drop), and the mixture is then heated at 100° for 2 hours, after which it is fractionally distilled, giving 3.5 g of β-diethylphosphoneisobutyramide (Table 1, compound 1). The residue in the distilling flask was a tarry mass.

Found % P 13.8; 13.8

$C_8H_{18}O_4NP$. Calculated % P 13.9

Addition of dipropylphosphorous acid to methacrylamide

7.8 g of dipropylphosphorous acid and 4 g of methacrylamide with sodium propoxide gave 2 g of β-dipropylphosphoneisobutyramide (Table 1, compound 2). Partial decomposition of the reaction product took place during distillation.

Found %: P 12.9

$C_{10}H_{22}O_4$ NP.

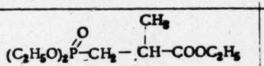
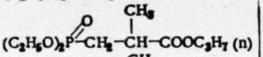
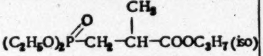
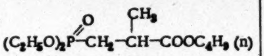
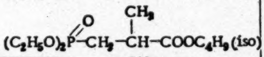
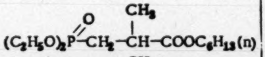
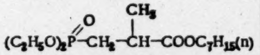
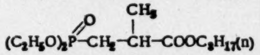
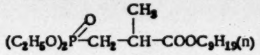
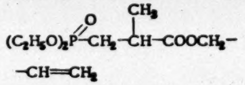
Calculated %: P 12.4

Addition of dibutylphosphorous acid to methacrylamide

9 g of dibutylphosphorous acid and 4 g of methacrylamide with sodium butoxide gave 2.4 g of β-dibutylphosphoneisobutyramide (Table 1, compound 3).

Found %: P 11.0; 10.80. $C_{12}H_{26}O_4NP$. Calculated %: P 11.1

TABLE 3

Serial No.	Formula	B.p. °C/p in mm	n_D^{20}	d_4^{20}	Yield %
1	 $(C_2H_5O)_2\overset{O}{\overset{/\!/}{P}}-CH_2-\overset{CH_3}{\overset{\mid}{C}}H-COOC_2H_5$	119-119.5/4	1.4339	1.0786	53
2	 $(C_2H_5O)_2\overset{O}{\overset{/\!/}{P}}-CH_2-\overset{CH_3}{\overset{\mid}{C}}H-COOC_3H_7$ (n)	125-126/4	1.4342	1.0698	69
3	 $(C_2H_5O)_2\overset{O}{\overset{/\!/}{P}}-CH_2-\overset{CH_3}{\overset{\mid}{C}}H-COOC_3H_7$(iso)	113-114/4	1.4330	1.0797	59
4	 $(C_2H_5O)_2\overset{O}{\overset{/\!/}{P}}-CH_2-\overset{CH_3}{\overset{\mid}{C}}H-COOC_4H_9$ (n)	140-142/4	1.4362	1.0508	44
5	 $(C_2H_5O)_2\overset{O}{\overset{/\!/}{P}}-CH_2-\overset{CH_3}{\overset{\mid}{C}}H-COOC_4H_9$(iso)	135-136/4	1.4362	1.0510	51
6	 $(C_2H_5O)_2\overset{O}{\overset{/\!/}{P}}-CH_2-\overset{CH_3}{\overset{\mid}{C}}H-COOC_6H_{13}$(n)	147-148/4	1.4392	1.0467	26
7	 $(C_2H_5O)_2\overset{O}{\overset{/\!/}{P}}-CH_2-\overset{CH_3}{\overset{\mid}{C}}H-COOC_7H_{15}$(n)	158-160/2,5	1.4410	1.0107	19
8	 $(C_2H_5O)_2\overset{O}{\overset{/\!/}{P}}-CH_2-\overset{CH_3}{\overset{\mid}{C}}H-COOC_8H_{17}$(n)	163-164/2,5	1.4419	1.0010	25
9	 $(C_2H_5O)_2\overset{O}{\overset{/\!/}{P}}-CH_2-\overset{CH_3}{\overset{\mid}{C}}H-COOC_9H_{19}$(n)	169-170/2,5	1.4421	0.9932	9
10	 $(C_2H_5O)_2\overset{O}{\overset{/\!/}{P}}-CH_2-\overset{CH_3}{\overset{\mid}{C}}H-COOCH_2-$ $-CH{=}CH_2$	117-119/2,5	1.4396	1.0799	41

Addition of dihexylphosphorous acid to methyl methacrylate

A solution (not saturated) of sodium hexoxide in hexanol was added gradually to 12.5 g of dihexylphosphorous acid and 5 g of methyl methacrylate, in an Arbuzov flask. Addition of sodium hexoxide was initially followed by evolution of heat, which no longer occurred after about 15 drops had been added. The mixture was then heated at 100° for 2 hours, and fractionally distilled, giving 3.3 g of methyl β-dihexylphosphoneisobutyrate (Table 2, compound 1).

Found %: P 8.9; 9.2

$C_{17}H_{35}O_5P$. Calculated %: P 8.9

Addition of diheptylphosphorous acid to methyl methacrylate

15 g of diheptylphosphorous acid and 5.4 g of methyl methacrylate with sodium heptoxide gave 2.5 g of methyl β-diheptylphosphoneisobutyrate.

Found %: P 7.7; 7.5

$C_{19}H_{39}O_5P$. Calculated %: P 8.2

Addition of dioctylphosphorous acid to methyl methacrylate

10 g of dioctylphosphorous acid and 3.3 g of methyl methacrylate with sodium octoxide gave 2.5 g of methyl β-dioctylphosphoneisobutyrate (Table 2, compound 3).

Found %: P 7.6; 7.5

$C_{21}H_{43}O_5P$. Calculated %: P 7.6

Addition of diethylphosphorous acid to esters of methacrylic acid

The esters used were prepared by trans-esterification of methyl methacrylate.

Ethyl methacrylate. Sodium ethoxide was added very gradually to 8 g of ethyl methacrylate and 9.7 g of diethylphosphorous acid, about 10 drops being added in all. Distillation of the reaction mixture gave 9.4 g of ethyl β-diethylphosphoneisobutyrate (Table 3, compound 1).

Found %: P 12.4; 12.1

$C_{10}H_{21}O_5P$. Calculated %: P 12.3

Propyl methacrylate. 7 g of propyl methacrylate and 7.7 g of diethylphosphorous acid similarly gave 10.2 g of propyl β-diethylphosphoneisobutyrate (Table 3, compound 2).

Found %: P 11.5; 11.6

$C_{11}H_{23}O_5P$. Calculated %: P 11.6

Isopropyl methacrylate. 7 g of isopropyl methacrylate and 7.6 g of diethylphosphorous acid gave 8.5 g of isopropyl β-diethylphosphoneisobutyrate (Table 3, compound 3).

Found %: P 11.3; 11.7

$C_{11}H_{23}O_5P$. Calculated %: P 11.6

Butyl methacrylate. 8 g of butyl methacrylate and 8 g of diethylphosphorous acid gave 6.9 g of butyl β-diethylphosphoneisobutyrate (Table 3, compound 4).

Found %: P 10.9; 10.9

$C_{12}H_{25}O_5P$. Calculated %: P 11.1

Isobutyl methacrylate. 6.2 g of diethylphosphorous acid and 6.2 g of isobutyl methacrylate gave 5.8 g of isobutyl β-diethylphosphoneisobutyrate (Table 3, compound 5).

Found %: P 11.5; 11.6

$C_{12}H_{25}O_5P$. Calculated %: P 11.1

Hexyl methacrylate. 8 g of diethylphosphorous acid and 9 g of hexyl methacrylate gave 2.3 g of hexyl β-diethylphosphoneisobutyrate (Table 3, compound 6).

Found %: P 10.3

$C_{14}H_{29}O_5P$. Calculated %: P 10.1

Heptyl methacrylate. 6 g of diethylphosphorous acid and 8 g of heptyl methacrylate gave 3.6 g of heptyl β-diethylphosphoneisobutyrate (Table 3, compound 7).

Found %: P 9.7; 9.6

$C_{15}H_{31}O_5P$. Calculated %: P 9.9

Octyl methacrylate. 7 g of diethylphosphorous acid and 10 g of octyl methacrylate gave 4.5 g of octyl β-diethylphosphoneisobutyrate (Table 3, compound 8)

Found %: P 8.8
$C_{16}H_{33}O_5P$. Calculated %: P 9.2

Nonyl methacrylate. 6.2 g of diethylphosphorous acid and 10 g of nonyl methacrylate gave 2.4 g of nonyl β-diethylphosphoneisobutyrate (Table 3, compound 9).

Found %: P 8.9; 8.5
$C_{17}H_{35}O_5P$. Calculated %: P 8.8

Allyl methacrylate. 5.2 g of diethylphosphorous acid and 5 g of allyl methacrylate gave 6.2 g of allyl β-diethylphosphoneisobutyrate (Table 3, compound 10).

Found %: P 11.5; 11.4.
$C_{11}H_{21}O_5P$. Calculated %: P 11.7

SUMMARY

1. Dialkylphosphorous acids add on to methacrylamide, to give dialkylphosphoneisobutyramides.

2. The products of addition of higher dialkylphosphorous acids to methyl methacrylate, and of diethylphosphorous acid to alkyl methacrylates are described.

LITERATURE CITED

[1] A. N. Pudovik. J. Gen. Chem., 22, 462 (1952). *

[2] A. N. Pudovik and B. A. Arbuzov. J. Gen. Chem., 21, 1837 (1951). **

Received March 29, 1952

A. E. Arbuzov Institute of Chemistry
Kazan Branch Academy of Sciences, U.S.S.R.

---

* See Consultants Bureau English Translation, page 565.
** See Consultants Bureau English Translation, p. 2055.

RESEARCHES IN THE FIELD OF PHOSPHORUS-ORGANIC COMPOUNDS

REACTION OF SULFIDES OF PHOSPHORUS WITH ALCOHOLS

M. I. Kabachnik and T. A. Mastryukova

The majority of methods for synthesis of phosphorus organic compounds, and in particular of esters and other derivatives of thio-acids of phosphorus, are based on the use of chloro-derivatives of phosphorus as starting products. This entails certain inconveniences, since halogen derivatives of phosphorus are sensitive to moisture, as a result of reaction with which from one to three (five) moles of hydrogen chloride or other halide are produced, and have to be removed from the sphere of reaction. Sulfides of phosphorus do not present these disadvantages, and are increasingly occupying the attention of chemists, as starting products for the synthesis of esters of thioacids of phosphorus. Up till now, however, the only sulfide used for this purpose has been P_4S_{10} (P_2S_5).

The reaction of phosphorus decasulfide with ethanol has been studied by Pishchimuka [1], who showed that the basic product is diethyl dithiophosphate:

$$P_2S_5 + 4C_2H_5OH \longrightarrow 2(C_2H_5O)_2PSSH + H_2S.$$

Nothing is known of the behavior of the lower sulfides of phosphorus in this respect. We have studied the reactions with alcohols of the sulfides P_4S_5, P_4S_6, and P_4S_7 (and also the product of fusing together a 1:1 molecular mixture of phosphorus and sulfur), and we found that these sulfides can serve for the preparation not only of products of the type $(RO)_2PSSH$, as was shown by Pishchimuka for the sulfide P_4S_{10} but also for various other classes of phosphorus thio-acid derivatives, including those of tervalent phosphorus.

The heptasulfide P_4S_7 reacts with lower alcohols in the cold, and with higher ones when heated. The products are a mixture of liquid substances, and hydrogen sulfide is evolved, with an admixture of phosphine. Fractionation of the products obtained with ethanol, propanol, and n-butanol gives three distinct fractions, of which the highest b.p. one is the ester of dithiophosphoric acid of the composition $(RO)_2(RS)PS$. The middle fraction appears to belong to the known series of partial esters of dithiophosphoric acid of the structure $(RO)_2PSSH$, and the lowest b.p. fraction consists of partial ester of thiophosphorous acid $(RO)_2PSH$.

The sulfide P_4S_7 reacts somewhat differently with methanol, giving only two products, trimethyl dithiophosphate $(CH_3O)_2(CH_3S)PS$ and dimethyl thiophosphite $(CH_3O)_2PSH$.

The formation of the three products $(RO)_2PSH$, $(RO)_2PSSH$, and $(RO)_2(RS)PS$, together with hydrogen sulfide and small amounts of phosphine and phosphorus, from the reaction between P_4S_7 and alcohols testifies to the complex nature of this reaction, and possibly to the existence of several parallel reactions proceeding simultaneously. We would here refer to the complex nature of the reaction of hydrolysis of the sulfide P_4S_7 [2].

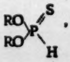
TABLE 1

Formula	B.p., °C/p in mm	d_4^{20}	n_D^{20}	MR*		Yield** %
				Found	Calc.	
$(CH_3O)_2PSH$	52-53.5/16.5	1.1892	1.4768	29.93	29.78	5.8
$(C_2H_5O)_2PSH$	67.5-68.5/12	1.0828	1.4597	38.91	39.02	14.5
$(n\text{-}C_3H_7O)_2PSH$	62-63/3	1.0290	1.4581	48.27	48.26	19.0
$(iso\text{-}C_3H_7O)_2PSH$	49-50/3	1.0135	1.4541	48.64	48.26	21.8
$(n\text{-}C_4H_9O)_2PSH$	89-90/4	0.9974	1.4583	57.48	57.50	20.8

The triesters of monothiophosphorous acid have previously been described by Arbuzov and Nikanorov [3], while the diesters $(RO)_2PSH$ have not previously been prepared; their properties are given in Table 1, below.

The dialkyl thiophosphites

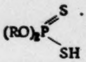
---

* The calculated MR is derived from the formula , taking the constants found by one of us [4]; as for thioketones, the atomic refractivity of sulfur was taken as being 9.70.

** Molar-percentage of phosphorus contained in P_4S_7 and converted into $(RO)_2PSH$.

are colorless, mobile liquids with a characteristic odor. They are soluble in organic solvents and in aqueous alcohol, giving solutions neutral to litmus. They are insoluble in water, and are hydrolyzed by acids and alkalis, and readily oxidized by nitric acid. The tervalent phosphorus content was determined by alkaline hydrolysis followed by heating with hydrochloric acid, in order to eliminate hydrogen sulfide, and then by treatment with mercuric chloride. Dialkyl thiophosphites react with sodium, with evolution of hydrogen.

The structure of the second product of reaction of phosphorus heptasulfide with alcohols appears from the analytical data, the results of titration, and cryoscopic determination of molecular weight, to correspond with the formula



$(RO)_2P(=S)SH$

. Substances of this structure have been known for over 90 years, but all the workers who obtained them described them an undistillable syrups, only the salts being taken for analysis. It was natural to suppose that our esters, which could readily be distilled in vacuum, were isomeric with the known dialkyl thiophosphates; we found, however, that our esters $(RO)_2PSSH$ had identical chemical properties with the known esters of dithiophosphoric acid. The lead salt prepared from our diethyl dithiophosphate was found to be identical with the known lead salt $[(C_2H_5O)_2PSS]_2Pb$, prepared according to Mastin and co-workers [6], by the reactions:

$$(C_2H_5O)_2PSCl + KSH \rightarrow (C_2H_5O)_2PSSK + HCl.$$

$$2(C_2H_5O)_2PSSK + Pb(CH_3COO)_2 \rightarrow [(C_2H_5O)_2PSS]_2Pb + 2CH_3COOK.$$

Both salts melted at 74.5 - 75.5°, mixed m.p. 75-76°. It is concluded that our dialkyl dithiophosphates have the formula $(RO)_2PSSH$; they were first prepared by us in a pure form. The constants of our esters are given in Table 2.

TABLE 2

Formula	B.p. °C/p in mm	d_4^{20}	n_D^{20}	MR*		Yield %
				Found	Calc.	
$(C_2H_5O)_2PSSH$	97-98/12	1.1650	1.5105	47.68	47.58	15.4
$(n\text{-}C_3H_7O)_2PSSH$	85-86/3	1.1040	1.4987	56.88	56.82	6.5
$(iso\text{-}C_3H_7O)_2PSSH$	70.5-71.5/3	1.0913	1.4920	56.89	56.82	25.4

* $AR_{S=} = 9.70$; $AR_{S-} = 9.34$

The dialkyl dithiophosphates are colorless, mobile, highly refractive liquids, with a smell of hydrogen sulfide. They are soluble in organic solvents and in aqueous alkalis. They can be titrated as strong acids in aqueous and alcoholic solution.

Triethyl dithiophosphate $(C_2H_5O)_2PS(SC_2H_5)$ has been synthesized by Pishchimuka [1] in two ways:

$$a)\ (C_2H_5S)PSCl_2 + 2C_2H_5OH \rightarrow (C_2H_5S)PS(OC_2H_5)_2 + 2HCl.$$

$$b)\ [(C_2H_5O)_2PSS]_2Pb + 2C_2H_5I \rightarrow 2(C_2H_5O)_2PS(SC_2H_5) + PbI_2.$$

The highest b.p. fraction obtained by us from the reaction between P_4S_7 and ethanol has the same physical constants as does Pishchimuka's triethyl dithiophosphate, which we also prepared by reaction (b) above. Table 3, below, gives the physical constants of the ester $(C_2H_5O)_2PS(SC_2H_5)$, prepared in different ways.

TABLE 3

Method of preparation	Author	B.p. °C/p in mm	d	n_D^{20}
$P_4S_7 + C_2H_5OH$	This paper	115-115.5/10	d_4^{20} 1.1168 d_4^{1} 1.1383	1.5013
$P_4S_{10} + C_2H_5OH$ through the Pb salt + C_2H_5I	" "	116-117/12	d_4^{20} 1.1156	1.5034
Ditto	Pishchimuka	128/20	d_0^{0} 1.1340	–

In order finally to show the identity of the esters obtained by both methods we prepared the double salt with mercuric iodide, of the composition $(C_2H_5O)_2PS(SC_2H_5)$, $2HgI_2$. These salts all melted at 85-86°, alone or in mixtures.

Table 4 gives the descriptions of the trialkyl dithiophosphates prepared by us by the reaction between P_4S_7 and alcohols.

Two series of products were obtained from the reaction between phosphorus hexasulfide P_4S_6* and methanol, ethanol, or propanol, viz., the dialkylthiophosphites $(RO)_2PSH$ and the trialkyl dithiophosphates $(RO)_2PS(SR)$; the acid esters $(RO)_2PSSH$ were not obtained at all. Phosphorus hexasulfide P_4S_6 also gives two products with isopropanol, these being $(iso\text{-}C_3H_7O)_2PSH$ and $(iso\text{-}C_3H_7O)_2PSSH$; triisopropyl dithiophosphate is not formed in this case. Phosphorus pentasulfide P_4S_5 gave two products with ethanol, viz $(C_2H_5O)PSH$ and $(C_2H_5O)_2PS(SC_2H_5)$, and the same products were given by a phosphorous-sulfur melt of the composition P_4S_4, although the yields were much lower than with P_4S_7 or P_4S_6.

---

* It cannot yet be taken as absolutely certain that the sulfide P_4S_6 exists. Giran [8] believes that an individual substance of this composition exists, but Mai [9] found that prolonged crystallization of a melt of the composition P_4S_6 gave the sulfide P_4S_7. Pernert and Brown [10] believe, on the basis of published work, that the sulfide P_4S_6 is not an individual substance.

TABLE 4

Formula	B.p. °C/p in mm	d_4^{20}	n_D^{20}	Parachor		MR*		Yield, %
				Found	Calc.	Found	Calc.	
$(CH_3O)_2PS(SCH_3)$	101-101.5/16.5	1.2415	1.5292	343.7	341.8	42.74	42.74	42.3
$(C_2H_5O)_2PS(SC_2H_5)$	115-115.5/10	1.1168	1.5013	460.4	457.8	56.65	56.60	11.0
$(n\text{-}C_3H_7O)_2PS(SC_3H_7)$	115-116/3	1.0561	1.4955	565.6	576	70.75	70.46	6.2
$(iso\text{-}C_3H_7O)_2PS(SC_3H_7)$	91-92/3	1.0351	1.4843	–	–	70.80	70.46	3.1
$(n\text{-}C_4H_9O)_2PS(SC_4H_9)$	148-149/4	1.0159	1.4859	–	–	84.20	84.32	9.5

* In calculation of MR we took for sulfur $AR_{S=} = 9.70$ and $AR_{S-} = 8.84$.

EXPERIMENTAL

Reaction of Alcohols with Sulfides of Phosphorus

The reactions were conducted in flasks fitted with reflux condensers and calcium chloride tubes. The lower alcohols began to react without heating, but the reaction was in all cases completed on a boiling water bath. The mixture was then filtered, excess of alcohol was distilled off from the filtrate, and the residue was fractionally distilled 3-4 times in a stream of carbon dioxide. The sulfides of phosphorus were prepared in the usual way, by melting together appropriate amounts of sulfur and red phosphorus, in an iron crucible [8].

Reaction of P_4S_7 with methanol. 52.2 g of sulfide P_4S_7 and 57.6 g of absolute methanol were allowed to react, and the product was 3 times fractionally distilled, at 16.5 mm., giving the fractions:

Fr. I. B.p. 53-53.5°/16.5 mm; 4.3 g; d_4^{20} 1.1892; n_D^{20} 1.4768

Found %: C 19.17; 19.24; H 5.43; 5.30; P 24.52; 24.42; MR 29.93
$C_2H_7O_2PS$. Calculated %: C 19.05; H 5.55; P 24.60; MR 29.78

Fr. II. B.p. 53.5-101°/16.5 mm; 3.7 g; a mixture.

Fr. III. B. p. 101-101.5°/16.5 mm; 43.0 g; d_4^{20} 1.2415; n_D^{20} 1.5292; σ_{20} 37.88 dynes/cm

Found %: C 21.07; 20.78; H 5.13; 5.38; P 17.90; 18.22; MR 42.74; P 343.7
$C_3H_9O_2PS_2$. Calculated %: C 20.93; H 5.22; P 18.04; MR 42.74; P 342.0

Reaction of P_4S_8 with methanol. 47.4 g of the sulfide P_4S_8 and 60.4 g of methanol gave the following fractions after two distillations at 8 mm:

Fr. I. B.p. 44-45°/8 mm; 5.1 g; n_D^{20} 1.4765; $(CH_3O)_2PSH$
Fr. II. B.p. 45-86°/8 mm; 2.1 g; a mixture
Fr. III. B.p. 86-87°/8 mm; 19.7 g; n_D^{20} 1.5272; $(CH_3O)_2PS(SCH_3)$

Reaction of P_4S_7 with ethanol. 58 g of sulfide P_4S_7 and 80 g of ethanol give, after four redistillations, the following fractions:

Fr. I. B.p. 67.5-68.5°/12 mm; 15.25 g; n_D^{20} 1.4597; d_4^{20} 1.0828 (compare experiment with P_4S_6); $(C_2H_5O)_2$ PSH
Fr. II. B.p. 68.5-97°/12 mm; 2.0 g; a mixture
Fr. III. B.p. 97-98°/12 mm; 19.1 g; n_D^{20} 1.5105; d_4^{20} 1.1650; σ_{20} 31.70 dynes/cm

Found %: C 25.83; 25.97; H 6.10; 6.12; P 16.53; 16.69; MR 47.68; P 378.8; MB (Mol. Wt. cryoscopically, in benzene) 182.7.
$C_4H_{11}O_2PS_2$. Calculated %: C 25.84; H 5.91; P 16.67; MR 47.58; P 379.8; MB 186.

Fr. IV. B.p. 98-115°/12-10 mm; 5.73 g; a mixture
Fr. V. B.p. 115-115.5°/10 mm; 15.8 g; n_D^{20} 1.5013; d_4^{20} 1.1168 (compare with experiment with P_4S_6) – $(C_2H_5O)_2(C_2H_5S)PS$

Lead diethyl dithiophosphate was obtained from 1.86 g of diethyl dithiophosphate and 1.64 g of lead acetate in neutral aqueous solution. Recrystallization from ethanol gave 2.0 g of white, finely crystalline salt, m.p. 75-76°.

Found %: C 16.68; 16.59; H 3.75; 3.50

$C_8H_{20}O_4P_2S_4Pb$. Calculated %: C 16.63 H 3.46

The same salt was prepared by the method of Mastin et al [6]; 6.6 g of diethyl thiophosphoryl chloride $(C_2H_5O)_2PSCl$, prepared according to Fletcher et al. [7] (b.p. 90.5-91.5°/19 mm.; n_D^{20} 1.4705; d_4^{20} 1.1899) was added drop by drop to an alkaline solution of potassium hydrosulfide (from 3.5 g of KOH), the mixture was heated on a water bath for 2 hours, the solution was filtered, and the filtrate was evaporated down. The residue was treated with lead acetate, and the lead salt so obtained was recrystallized, giving 1.8 g of colorless, finely crystalline salt, m.p. 74.5-75.5°; published values for m.p. 74° [6], 74° [7], mixtures gave no depression of m.p.

Ethylation of lead diethyl dithiophosphate (by Pishchimuka's method). 10 g of the lead salt of the diethyl ester obtained from an experiment with P_4S_7 was heated with 5.6 g of ethyl iodide for 90 minutes on a water bath, the solution was filtered off from the lead iodide which forms, and the filtrate was fractionally distilled, giving 6.1 g (82.3% yield) of triethyl dithiophosphate, b.p. 116-117°/12 mm; n_D^{20} 1.5034; d_4^{20} 1.1156.

Double Salt of Mercuric Iodide and Triethyl Dithiophosphate $(C_2H_5H)_2PS(SC_2H_5)\cdot 2HgI_2$

a) From the ester obtained from P_4S_7. 10.7 g of triethyl dithiophosphate was heated in an oil bath at 95-110° with 45.4 g of mercuric iodide, for 80 min., and the product was recrystallized from alcohol, giving 39.0 g of double salt, m.p. 79-82°, rising to 85-86° after a second recrystallization.

b) From the ester obtained from ethylation of lead diethyl dithiophosphate. The m.p. was 85-86°, mixed m.p. with above product, 85-86°; Pishchimuka gives an m.p. of 86°.

Reaction of P_4S_6 with ethanol. 50.8 g of the sulfide P_4S_6 and 69 g of absolute ethanol were allowed to react, and the product was distilled three times, giving the fractions:

Fr. I. B.p. 63-65.5°/11 mm; 2.5 g
Fr. II. B.p. 65.5-66.5°/11 mm; 26.3 g; n_D^{20} 1.4592; d_4^{20} 1.0825.

Found %: C 31.35; 31.18; H 7.13; 7.30; S 20.55; 20.45; P 20.35; 20.35; MR 38.91.

$C_4H_{11}O_2PS$. Calculated %: C 31.17; H 7.07; S 20.78 P 20.13; MR 39.02

Fr. III. B.p. 66.5-110°/9-11 mm; 2.5 g; a mixture
Fr. IV. B.p. 110-111°/9 mm; 20.1 g; n_D^{20} 1.5015; d_4^{20} 1.1165; d_4^1 1.1383; σ_{20} 33.09 dynes/cm.

Found %: C 33.78; 34.00; H 7.17; 7.30; S 29.85; 30.09; P 14.69; 14.37; MR 56.65; P 460.4;
M (cryoscopic, in benzene) 209.9

$C_6H_{15}O_2PS_2$. Calculated %: C 33.64; H 7.01; S 29.95; P 14.49; M 56.60; P 459.0; M 214.

Determination of tervalent phosphorus in Fraction II, $(C_2H_5O)_2PSH$. A weighed amount of diethyl thiophosphite was dissolved in 20 ml of 0.1N-NaOH, and the solution was heated in a Kjeldahl flask for 10 hours, passing a stream of CO_2. It was then made acid with 0.1N·HCl, and boiled in a stream of CO_2 until the emerging gas no longer contained hydrogen sulfide, after which phosphorous acid was oxidized with mercuric chloride, in the usual way. The calomel formed was collected, washed and dried at 105°.

Found %: P 20.25; 20.17

$C_4H_{11}O_2PS$. Calculated %: P 20.13

Reaction of P_4S_5 with ethanol. 28.4 g of the sulfide P_4S_5 was heated for 10 hours with 46.0 g of absolute ethanol, the solution was filtered from the solid residue, which weighed 7.4 g, and the filtrate was fractionated (3 distillations) at 9.5 mm, giving the fractions:

Fr. I. B.p. 59.5-61°/9.5 mm; 0.9 g
Fr. II. B.p. 61-61.5°/9.5 mm; 8.3 g; n_D^{20} 1.4589; d_4^{20} 1.0805

Found MR 38.96; Calculated MR 39.02 $(C_2H_5O)_2PSH$

Fr. III. 61.5-105°/9.5 mm; 3.4 g; a mixture
Fr. IV. 105-105.5°/9.5 mm; 9.3 g; n_D^{20} 1.5020; d_4^{20} 1.1157.

Found MR 56.60; Calculated MR 56.60 $(C_2H_5O)_2PS(SC_2H_5)$

Reaction of 1:1 atomic sulfur-phosphorus melt with ethanol. 49.8 g of the melt was treated with 80 g of ethanol, and the solution was filtered after completion of the reaction (solid residue 17.3 g). The filtrate gave the following fractions after two distillations at 11 mm:

Fr. I B.p. 64-65.5°, 1.3 g
Fr. II B.p. 65.5-66.5, 16.3 g; n_D^{20} 1.4592 $(C_2H_5O)_2PSH$
Fr. III B.p. 66.5-112°, 7.0 g
Fr. IV B.p. 112-112.5°, 19.3 g; n_D^{20} 1.5031 $(C_2H_5O)_2PS(SC_2H_5)$

Reaction of P_4S_7 with propanol. 52.2 g of the sulfide P_4S_7 and 120 g of absolute n-propanol were taken. The product gave the following fractions after 4 distillations at 3 mm:

Fr. I B.p. 59-62°, 0.5 g.
Fr. II B.p. 62-63°, 20.8 g; n_D^{20} 1.4581; d_4^{20} 1.0290.

Found %: P 17.12; 17.20; MR 48.27
$C_6H_{15}O_2PS$. Calculated %: P 17.03; MR 48.26

Fr. III B.p. 63-85°, 4.6 g; a mixture
Fr. IV B.p. 85-66°; 8.3 g. n_D^{20} 1.4987; d_4^{20} 1.1040.

Found %: P 14.37; 14.45; MR 56.88
$C_6H_{15}O_2PS_2$. Calculated %: P 14.49; MR 56.82

Fr. V B.p. 86-115°; 3.7 g; a mixture
Fr. VI B.p. 115-116°, 11.0 g; n_D^{20} 1.4955; d_4^{20} 1.0561; σ_{20} 29.91 dynes/cm

Found %: P 12.02; 12.21; MR 70.75; P 565.6
$C_9H_{21}O_2PS_2$. Calculated %: P 12.11; MR 70.46; P 576.0

Reaction of P_4S_6 with n-propanol. 47.4 g of the sulfide P_4S_6 and 108 g of n-propanol give a product, which after three vacuum distillations at 4 mm gave the fractions:

Fr. I B.p. 74.5-75.5°, 30.2 g; n_D^{20} 1.4581; d_4^{20} 1.0290

Found MR 48.27
$C_6H_{15}O_2PS$. Calculated MR 48.26

Fr. II B.p. 75.5-123°; 6.0 g; a mixture
Fr. III B.p. 123-124°, 9.7 g; n_D^{20} 1.4952; d_4^{20} 1.0561

Found MR 70.71
$C_9H_{21}O_2PS_2$. Calculated MR 70.46

Reaction of P_4S_7 with isopropanol. 52.2 g of the sulfide P_4S_7 and 120 g of isopropanol give a product, from which the following fractions were obtained, at 3 mm:

Fr. I B.p. 48-49°, 0.5 g
Fr. II B.p. 49-50°, 23.8 g; n_D^{20} 1.4541; d_4^{20} 1.0135.

Found %: P 17.10; 17.13; S 17.55; 17.55; MR 48.64
$C_6H_{15}O_2PS$. Calculated %: P 17.03 S 17.58; MR 48.26

Fr. III B.p. 50-70.5°;3.8 g; a mixture
Fr. IV B.p. 70.5-71.5°, 32.6 g; n_D^{20} 1.4920; d_4^{20} 1.0913

Found %: P 14.40; 14.46; S 29.62; 29.35; MR 56.89
$C_6H_{15}O_2PS_2$. Calculated %: P 14.49; S 29.91; MR 56.82

Fr. V B.p. 71.5-91°, 3.7 g; a mixture
Fr. VI B.p. 91-92°, 4.7 g; n_D^{20} 1.4843; d_4^{20} 1.0351

Found %: S 24.95; 25.17
$C_9H_{21}O_2PS_2$. Calculaed %: S 25.00

Reaction of P_4S_6 with isopropanol. 47.4 g of the sulfide P_4S_6 and 108 g of isopropanol gave a product, from which the following fractions were obtained after three distillations:

Fr. I B.p. 47-48°/3 mm; 26.0 g; n_D^{20} 1.4533; d_4^{20} 1.0132 (iso-$C_3H_7O)_2PSH$
Fr. II B.p. 48-96°/3-7mm; 5.5g; a mixture
Fr. III B.p. 96-97°/7 mm; 4.0 g; n_D^{20} 1.4936; d_4^{20} 1.0921 (iso-$C_3H_7O)_2PSSH$

Reaction of P_4S_7 with n-butanol. 52.2 g of the sulfide P_4S_7 and 133.2 g of n-butanol were allowed to react, and the product was distilled at 4 mm., giving the fractions:

Fr. I B.p. 101-105°, 29.0 g
Fr. II B.p. 105-110°, 20.5 (with decomposition)

Decomposition then became increasingly more intense, so that distillation was stopped, leaving 57 g of a bright yellow syrup in the flask; this residue was treated separately. The distillates were redistilled three times at 4 mm, giving

Fr. I B.p. 89-90°, 26.2 g; n_D^{20} 1.4583; d_4^{20} 0.9974.

Found %: P 14.62; 14.53; MR 57.48
$C_8H_{19}O_2PS$. Calculated %: P 14.76; MR 57.50

Fr. II B.p. 90-148°, 4.3 g; a mixture
Fr. III B.p. 148-149°, 13.4 g; n_D^{20} 1.4859; d_4^{20} 1.0159

Found %: P 10.52; 10.50; MR 84.20
$C_{12}H_{27}O_2PS_2$. Calculated %: P 10.40 MR 84.32

The undistilled residue was treated with a small excess of 0.1 N NaOH, and the aqueous layer was separated from the oil, and extracted with ether. The ethereal extract was added to the oil, and the solution was dried with calcium chloride; it yielded a further 3.6 g of tributyl dithiophosphate, b.p. 148-149°/4 mm; n_D^{20} 1.4863.

The aqueous layer was evaporated down on the water bath, and excess of aqueous mercuric chloride was added. The precipitate was thrice recrystallized from alcohol, giving 4.9 g of mercury dibutyl dithiophosphate, m.p. 60-61°. The same salt was prepared by the method of Mastin et al [7], also m.p. 60-61°, mixed m.p. with our salt 60-60.5°.

SUMMARY

1. A study has been made of the reactions of the sulfides of phosphorous P_4S_7, P_4S_6 and P_4S_5 with alcohols.

2. Three types of products are obtained from P_4S_7 and ethanol, propanol or butanol, viz., $(RO)_2PSH$, $(RO)_2PSSH$, and $(RO)_2(RS)PS$.

3. The sulfide P_4S_7 and methanol give the esters $(CH_3O)_2PSH$ and $(CH_3O)_2(CH_3S)PS$.

4. The sulfide P_4S_6 reacts with alcohols to give esters of the types $(RO)_2PSH$ and $(RO)_2(RS)PS$. Only with isopropanol does this sulfide give the esters (iso-$C_3H_7O)_2PSH$ and (iso-$C_3H_7O)_2PSSH$.

5. The same products are obtained from the sulfide P_4S_5, or the 1:1 atomic sulfur-phosphorus melt, and alcohols as with the sulfide P_4S_6, but the yields are lower.

6. The dialkyl dithiophosphates $(RO)_2PSSH$ have for the first time been prepared pure; they are liquids, which can be distilled in vacuum.

LITERATURE CITED

[1] P.S. Pishchimuka, J. Russ. Phys. Chem. Soc., 44, 1406 (1912); Ukrain. Chem. J., 1, 87 (1927). [2] W. D. Treadwell, Ch. Beeli, Helv. Chim. Acta, 18, 1161 (1935). [3] A.E. Arbuzov and K.A. Nikanorov, Proc. Acad. Sci., USSR, 12, No. 1, 75 (1948). [4] M.I. Kabachnik. Bull. Acad. Sci. USSR., Div. Chem. Sci. No. 2, 219 (1948). [5] P. Nylen, Studien uber organische Phosphorverbindungen, Uppsala, 1930. [6] J.W. Mastin, G.R. Norman and E.A. Wellmeunster, J. Am. Chem. Soc. 67, 1662 (1945). [7] J.H. Fletcher, J.C. Hamilton, J. Hechenbleikner, E.J. Hoegberg, B.J. Sertle, J.J. Cassaday, J. Am. Chem. Soc. 70, 3943 (1948). [8] M. H. Giran, Comptes rend., 142, 398 (1905). [9] J. Mai, Ann., 265, 192 (1891). [10] J. Pernert, J. H. Brown, Chem. Eng. News, 27, 2143-2146 (1949)

Received March 13, 1952

Institute of Organic Chemistry
Academy of Sciences U.S.S.R.

STUDIES IN THE FIELD OF CYANINE DYES

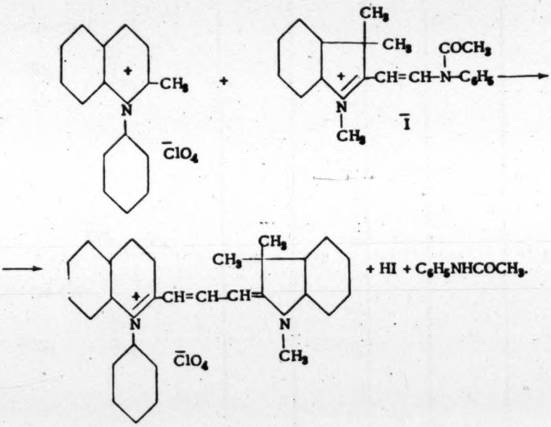
PART 3. ASYMMETRICAL CARBOCYANINES FROM N-ARYLQUINALDINE AND INDOLENINE

G. T. Pilyugin

The asymmetrical cyanines have only relatively recently been studied, owing chiefly to the much greater difficulty of preparing them, as compared with the symmetrical cyanines, which are of particular importance as sensitizers of silver bromide in photographic emulsions. The asymmetrical cyanines are thus of considerable interest, from both the theoretical and the practical points of view.

Asymmetrical cyanines containing an N-arylquinoline ring were first described by the author [1]. It is of interest, in studying the structure of this class of dyes, to investigate the effect on the color of the dye of varying the heterocyclic component and the substituent in various positions of the molecule.

We shall in the present paper consider asymmetrical cyanines formed from N-arylquinolinium salts and the intermediate product 2-β-anilinovinyl-3,3-dimethylindolenine methiodide [2]:



The N-arylquinoindocyanines obtained are shown in the Table, which also gives, for the sake of comparison, the absorption maxima of the corresponding symmetrical dyes.

The presence of N-aryl groups in the quinoline ring gives insignificant bathochromic shifting of the absorption maximum of the asymmetrical dyes, as compared with alkyl substituents. This led to the much smaller hypsochromic shift of the absorption maximum of the asymmetrical dye from the additive value of the maximum for the corresponding symmetrical dyes. Thus, for example, the dye obtained from the quaternary salt of quinaldine ethiodide and the intermediate product of indolenine has an absorption maximum at 559.5 mμ, and the hypsochromic shift of the maximum from the additive value amounts here to 15.0 mμ, whereas the analogous dye with a phenyl substituent has an absorption maximum at 572 mμ, and the hypsochromic shift from the additive value is here 7.5 mμ.

In comparing the dyes obtained with each other, taking as the basis for comparison the dye with a N-phenyl group (No. 1), we observe the following mutual effects of various structural groupings. Introduction of the methyl group into position 6 leads to a bathochromic shift of maximum absorption of 6 mμ (No. 2), whereas a 6-methyl

TABLE

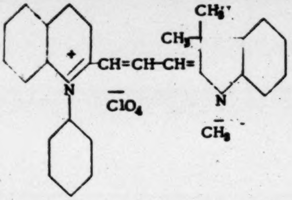
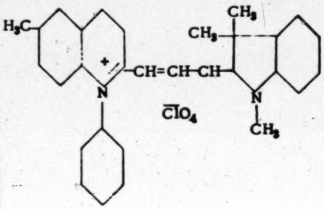
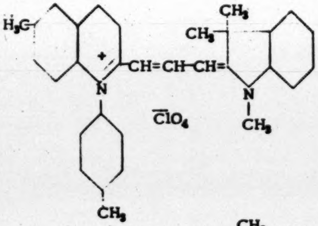
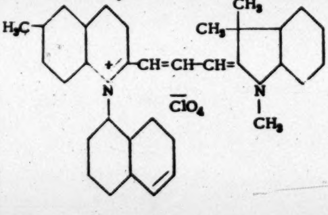
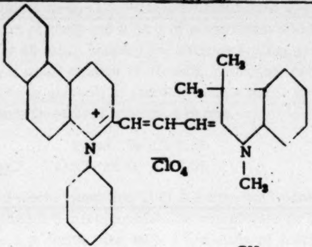
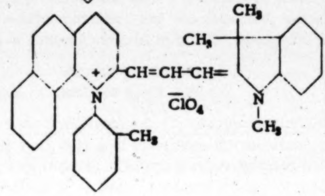
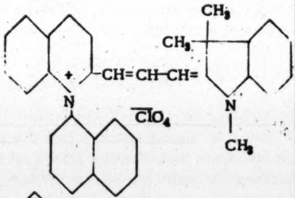
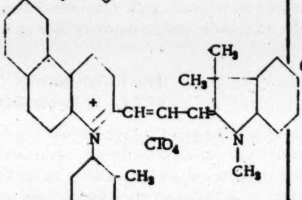
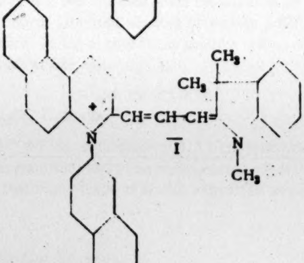
No.	Formula of dye	Absorption maximum, mμ				Deviation from addition rule	
	(I) (II)	Symmetrical from (I)	Symmetrical from (II)	Asymmetrical from $\frac{(I+II)}{2}$	Asymmetrical (found)	Hypsochromic	Bathochromic
1		614	545	579.5	572	7.5	–
2		620	545	582.5	578	4.5	–
3		622	545	583.5	572	11.5	–
4		625	545	585	580	5	–

TABLE (Continued)

Serial No.	Formula of dye (I) (II)	Absorption maximum, mμ Symmetrical from(I)	Symmetrical from(II)	Asymmetrical from $\frac{(I+II)}{2}$	Asymmetrical (found)	Deviation from addition rule Hypsochromic	Bathochromic
5	 CH₃ CH₃ + CH=CH-CH= N N ClO₄ CH₃	645	545	595	580	15	–
6	 CH₃ CH₃ + CH=CH-CH= N ClO₄ N CH₃ CH₃	642	545	543.5	585	8.5	–
7	 CH₃ CH₃ + CH=CH-CH= N ClO₄ N CH₃	618	545	581.5	574	7.5	–
8	 CH₃ CH₃ + CH=CH-CH= N ClO₄ N CH₃ CH₃	644	545	594.5	580	14.5	–
9	 CH₃ CH₃ + CH=CH-CH= N I N CH₃	654	545	599.5	585	14.5	–

group in the N-p-tolyl derivative has no effect on shift of the maximum (No. 3). A bathochromic shift of the absorption maximum of 8 mμ is found in the 6-methyl-N-naphthyl derivative (No. 4) and in the 5,6-benzo-N-phenyl derivative (No. 5), while the shift for the 7,8-benzo-N-o-tolyl derivative (No. 6) amounts to 13 mμ. Simultaneous presence of phenylene groups in the 5,6 position of the quinoline ring and in the N-aryl substituent (No. 9) gives a shift of 13 mμ. It is of interest that presence of a phenylene group in the N-aryl substituent has only a very small effect (No. 7); a similar finding has been reported for dyes of a symmetrical structure [3].

EXPERIMENTAL

(1-Phenylquinoline-2)-(1,3,3-trimethylindolenine-2)-trimethinecyanine perchlorate. 0.4 g of indolenine intermediate product (1 mol) and 0.34 g of phenylquinaldine perchlorate (1 mol. + 20% excess) were heated with 2 ml of pyridine for 30 min., keeping the mixture boiling gently. The dye was precipitated from the pyridine solution by adding a small amount of alcohol, collected, and washed with water, alcohol, and ether. The dye was recrystallized from alcohol, as platelets with a green metallic sheen, m.p. 180° (decomposition), yield 43%. Absorption maximum in ethanol solution 572 mμ.

Found %: Cl 6.94
$C_{29}H_{27}N_2O_4Cl$. Calculated %: Cl 7.05

(1-Phenyl-6-methylquinoline-2)-(1,3,3-trimethylindolenine-2)-trimethinecyanine perchlorate. 0.2 g of the quaternary salt 1-phenyl-6-methylquinaldine perchlorate in 2 ml of pyridine and 0.18 g of indolenine derivative were heated at the b.p. for 30 min. with a few drops of acetic anhydride. The dye was precipitated from the cooled solution by addition of ether, and was collected, washed with alcohol and ether, and recrystallized, giving 0.12 g (44% yield) of dark red crystals, m.p. 215°, absorption maximum at 578 mμ.

Found %: Cl 6.61
$C_{30}H_{29}N_2O_4Cl$. Calculated %: Cl 6.87

(1-p-Tolyl-6-methylquinoline-2)-(1,3,3-trimethylindolenine-2)-trimethinecyanine perchlorate. 0.25 g of quaternary salt (1.2 mol), 0.25 g of indolenine intermediate (1 mol) and 2 ml of pyridine were boiled under reflux for 30 min, with shaking. The dye was precipitated from the cooled solution by adding ether, and the precipitate was dissolved in alcohol. An equal volume of saturated aqueous potassium perchlorate was added to the solution, and the crystalline product was recrystallized from aqueous alcohol, giving light green crystals of m.p. 215-218° (decomposition), yield 27%, absorption maximum at 572 mμ.

Found %: Cl 6.32
$C_{31}H_{31}N_2O_4Cl$. Calculated %: Cl 6.69

(1-α-Naphthyl-6-methylquinoline-2)-(1,3,3-trimethylindolenine-2)-trimethinecyanine perchlorate. A mixture of 0.3 g of 1-α-naphthyl-6-methylquinaldine iodide, 0.26 g of indolenine intermediate, and 2 ml of pyridine is boiled for 1 hr, adding a few drops of acetic anhydride during the process. The reaction product was treated with ether, and the residue was dissolved in ethanol (2 ml). Saturated aqueous potassium perchlorate was added, the mixture was heated to boiling, and left for 24 hrs. giving 0.13 g (43% yield) of violet crystals, with a metallic sheen, m.p. 252° (decomposition), absorption maximum 580 mμ. Alcoholic solutions of the dye were colored violet.

Found %: Cl 6.41
$C_{34}H_{31}N_2O_4Cl$. Calculated %: Cl 6.26

(1-Phenyl-5,6-benzoquinoline-2)-(1,3,3-trimethylindolenine-2)-trimethinecyanine perchlorate. A mixture of 0.3 g of 2-β-acetanilidovinyl-1,3,3-trimethylindolenine iodide, 0.22 g of the quaternary salt of benzoquinaldine perchlorate, and 2 ml of pyridine, with a few drops of acetic anhydride, were boiled, with constant shaking, for 40 min. The dye was precipitated from the solution by adding ether, and the precipitate was dissolved in 2 ml of alcohol, 2 ml of saturated aqueous potassium perchlorate were added, and the product was recrystallized from aqueous alcohol, giving a crystalline product with a metallic sheen, m.p. 239° (decomposition), yield 29%, absorption maximum at 580 mμ.

Found %: Cl 6.16
$C_{33}H_{29}N_2O_4Cl$. Calculated %: Cl 6.42

(1-o-Tolyl-7,8-benzoquinoline-2)-(1,3,3-trimethylindolenine-2)-trimethinecyanine perchlorate. A mixture of 0.15 g of 2-β-acetanilidovinyltrimethylindolenine iodide, 0.25 g of 1-o-tolyl-7,8-benzoquinaldine perchlorate, 3 ml of pyridine, and a few drops of acetic anhydride was boiled for about 1 hr., cooled, ether was added, the

precipitate was collected, washed with water, alcohol, and ether, and recrystallized from aqueous alcohol, giving a product, m.p. 225° (decomposition), absorption maximum at 585 mμ. The alcoholic solution was colored lilac.

Found %: Cl 6.14
$C_{34}H_{31}N_2O_4Cl$. Calculated %: Cl 6.26

(1-α-Naphthylquinoline-2)-(1,3,3-trimethylindolenine-2)-trimethinecyanine perchlorate. A mixture of 0.2 g of the quaternary salt α-naphthylquinaldine perchlorate, 0.16 g of 2-β-acetanilidovinyltrimethylindolenine methiodide, 2 ml of pyridine, and a few drops of acetic anhydride was boiled for 45 min., 5 ml of ether was added to the cooled solution, the precipitate was dissolved in 2 ml of ethanol, 2 ml of saturated aqueous potassium perchlorate and 5 ml of water were added to the warm solution, which was then boiled for 5 min. The finely crystalline product was collected, washed with ether, and recrystallized from aqueous alcohol, giving 0.1 g of dark blue crystals, m.p. 260° (decomposition), yield 30%, absorption maximum at 574 mμ. The alcoholic solution of the dye was colored bluish red.

Found %: Cl 6.27
$C_{33}H_{29}N_2O_4Cl$. Calculated %: Cl 6.42

(1-o-Tolyl-5,6-benzoquinoline-2)-(1,3,3-trimethylindolenine-2)-trimethinecyanine perchlorate. A mixture of 0.2 g of indolenine intermediate, 0.22 g of the quaternary salt tolylbenzoquinaldine iodide, 2 ml of pyridine, and a few drops of acetic anhydride was boiled for 50 min, 5 ml of ether was added to the cooled solution, the precipitate was collected, dissolved in alcohol, and reprecipitated with ether. 2 Ml of saturated aqueous potassium perchlorate was added to a boiling alcoholic solution of the dye, and the salt was collected the next day, washed with alcohol and ether, and recrystallized from aqueous alcohol, giving 0.065 g (26.8% yield) of dark violet crystals with a metallic sheen, m.p. 225° (decomposition), absorption maximum 580 mμ.

Found %: Cl 6.08
$C_{34}H_{31}N_2O_4Cl$. Calculated %: Cl 6.26

(1-β-Naphthyl-5,6-benzoquinoline-2)-(1,3,3-trimethylindolenine-2)-trimethinecyanine iodide. A mixture of 0.4 g of indolenine intermediate (1 mol), 0.48 g of the quaternary salt naphthylbenzoquinaldine iodide (1 mol + 20% excess), 2 ml of pyridine, and 0.5 ml of acetic anhydride was boiled for 40 min. The color of the solution rapidly changed from reddish violet to blue. The dye was precipitated by the addition of ether to the cooled solution, and was recrystallized from aqueous alcohol; the yield of crude product was 0.21 g, or 37.5% which fell to 22% after recrystallization. Dark blue crystals, m.p. 248-250°, absorption maximum at 585 mμ.

Found %: I 20.38
$C_{37}H_{31}N_2I$. Calculated %: I 20.15

SUMMARY

1. New carbocyanine dyes with an asymmetrical structure have been prepared by the reaction of quaternary salts of N-arylquinaldine with indolenine intermediate product.

2. The properties of the new asymmetrical dyes have been studied.

Received December 1, 1951

Institute of Organic Chemistry
Academy of Sciences USSR
Chernovits State University

LITERATURE CITED

[1] G. T. Pilyugin, Bull. Acad. Sci. USSR, Div.Chem.Sci., No. 2, 253 (1952)*; Pilyugin and Z. Ya. Krainer, Proc. Acad. Sci., USSR, 81, 4, 609 (1951).

[2] T. Ogata, C. 1932, II, 711; Brit. Pat. 344409 (I.C.I.) 1931, I. 3297; H. A. Piggot, E. H. Rodd, US Pat. 2071898.

[3] G. T. Pilyugin, Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 3, 512, 520 (1952). **

---

* See Consultants Bureau English Translation, p. 347.

** See Consultants Bureau English Translation, p. 491, 499.

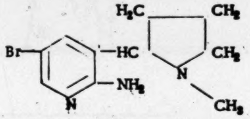
BLANK
PAGE

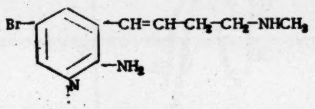
ULTRA-VIOLET ABSORPTION SPECTRA OF SOME DERIVATIVES OF PYRIDINE AND NICOTINE

PART 3 [1]

K. A. Zhukova, M. S. Kondakova, and Ya. L. Goldfarb

Goldfarb and Kondakova [2], acting on 5-bromo-2-aminonicotine (I) with acetic anhydride, obtained an isomer to which they assigned the structure (II), on the grounds that under similar conditions 2-amino-nicotine gives 2-aminometanicotine:


(I)


(II)

It was supposed that the action of acetic anhydride consists in the opening of the pyrrolidine ring of molecule (I), giving a new molecule with a double bond in the side-chain conjugated with those of the pyridine ring. This sort of change in the degree of unsaturation of the molecule involves, in particular, a bathochromic shift in the absorption spectrum [3]; for this reason the presence of such a shift, in comparing the absorption curves of 5-bromo-2-aminonicotine and of the new base derived from it, could be taken as confirmatory evidence that the latter is 5-bromo-2-aminometanicotine. For this reason we have undertaken the study of the ultra-violet absorption spectra of this compound, and of others of related structure. The same method of comparing spectra was later found useful in solving certain problems arising from a study of the transformations of 5-bromo-2-aminometanicotine (II). The results obtained are given in Table 1*, and the absorption curves serving as bases for comparison are shown in Figs. 1 and 2.

The first maximum of the absorption band of 2-aminometanicotine, the structure of which as a compound with a double bond in the side-chain conjugated with those of the pyridine ring has been established by chemical methods [4], is shifted in the long-wave part of the spectrum by about 25 mμ, as compared with the corresponding maximum of 2-aminonicotine. The absorption curve of 2-amino-3-(4'-dimethylamino-but-1'-enyl)-pyridine, which may be regarded as a methylation product of 2-aminometanicotine, scarcely differs with respect to the position and magnitude of the absorption maximum (Table 1) from that for the latter compound. Such a coincidence of the absorption spectra was to be expected, since the introduction of a methyl group, which itself does not perceptibly affect the absorption spectrum, does not in the given case involve any rearrangement of the double bonds.

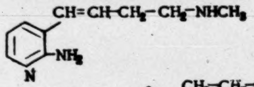
Hydrogenation of 2-aminometanicotine gives 2-amino-3-(4'-methylaminobutyl)-pyridine, in which both bands (Fig.1) are shifted in the direction of shorter wave-lengths, and the absorption curve becomes practically identical with those of 2-aminopyridine or 2-aminonicotine.

Systems of a higher degree of unsaturation than 2-aminometanicotine are represented by 2-amino-3-buta-1',3'-dienylpyridine (Fig.3), for which the maxima of the absorption bands are at 344 mμ (log E 4.11) and 270 mμ (log E 4.16), and are hence shifted considerably towards the red end of the spectrum, in comparison with the corresponding maxima for 2-aminometanicotine. Hydrogenation of the unsaturated side-chain again gave, as could be expected, a system (2-amino-3-butyl-pyridine) spectrally indistinguishable from 2-aminopyridine or 2-aminonicotine.

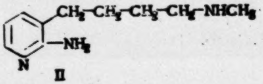
It is evident from the data cited that the changes in the absorption spectra of substituted 2-aminopyridines are of the same nature as in other systems, arranged in order of increasing number of conjugated double bonds, i.e., formation of a new conjugated double bond involves a considerable shift of the absorption bands in the direction of

---

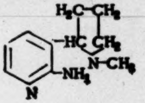
* The spectra are in all cases those obtained in ethanol solutions of the bases.



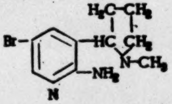
I



II



I



II

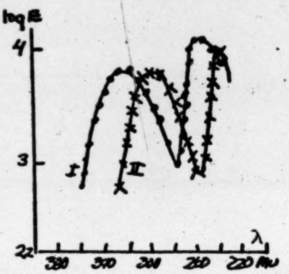


Fig. 1

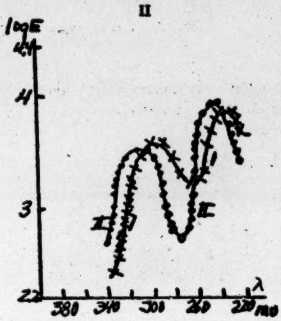


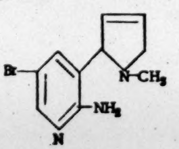
Fig. 2

longer wave lengths. A shift in the same direction, and of the same magnitude, is observed when we compare the spectra of 5-bromo-2-aminonicotine and of the base formed from it by the action of acetic anhydride (Fig. 4); this confirms our previously expressed view (loc. cit.) that this is 5-bromo-2-aminometanicotine, the first maximum of the absorption curve of which is at 335 mμ (log E 3.71). It thus appears that substitution of bromine in position 5 of the pyridine ring of 2-aminometanicotine leads to a further shift towards the red end of the spectrum, on the average of about 12 mμ.

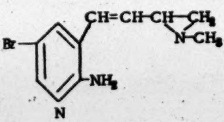
The absorption curves of 5-bromo-2-aminometanicotine and of the product of its ring closure, in which the partly hydrogenated ring retains a double bond conjugated with the double bond system of the second ring, viz., 6-bromo-2-methylaminomethyl-1,2-dihydro-1,8-naphthiridine, differ only in the position of the second maximum, but are identical in all other respects (Fig. 5). In view of this, the data for the absorption spectrum of 6-bromo-2-methyl-1,8-naphthiridine are the more noteworthy.

The absorption curve for this compound has a first maximum shifted towards the ultra-violet, as compared with the former dihydronaphthiridine (Fig. 6), with a second maximum ending abruptly at 245 mμ; these two systems have radically different spectra. This effect appears to be a consequence of dehydrogenation of dihydronaphthiridine, which leads to production of a radically new chromophore (1,8-naphthiridine), with a new system of double bonds.

While studying the transformation of 5-bromo-2-aminometanicotine we found ourselves obliged to choose between structures A and B for the base of m.p. 127-129°, formed together with 6-bromo-2-methylamino-methyl-1,2-dihydro-1,8-naphthiridine by the action of alkali on 5-bromo-2-amino-3-(3'-bromo-4'-methylaminobut-1'-enyl)-pyridine:



A



B

TABLE 1

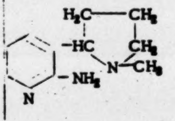
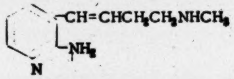
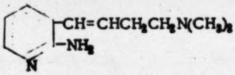
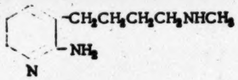
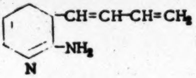
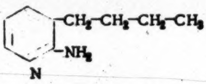
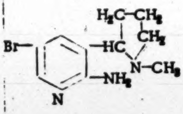
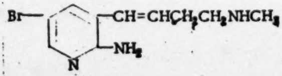
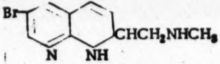
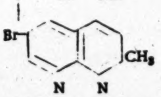
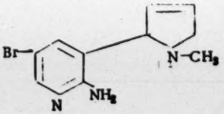
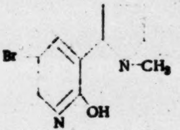
Substance	Formula	1st max.	log E	2nd max.	log E
2-Aminonicotine		298	3.56	235	3.85
2-Amino-3-(4'-methylaminobut-1'-enyl)-pyridine (2-aminometanicotine)		323	3.79	257	4.06
2-Amino-3-(4'-dimethylaminobut-1'-enyl)-pyridine		320	3.72	255	3.99
2-Amino-3-(4'-methylaminobutyl)-pyridine (2-aminodihydrometanicotine)		298	3.78	240	3.96
2-Amino-3-buta-1',3'-dienyl pyridine		344	4.11	270	4.16
2-Amino-3-butylpyridine		295	3.62	238	3.8
5-Bromo-2-aminonicotine		310	3.52	245	3.92
5-Bromo-2-amino-3-(4'-methylaminobut-1'-enyl)-pyridine (5-bromo-2-aminometanicotine)		335	3.71	255	3.92
6-Bromo-2-methylaminomethyl-1,2-dihydro-1,8-naphthiridine		336	3.66	238	3.98
6-Bromo-2-methyl-1,8-naphthiridine					
5-Bromo-2-amino-3-(1'-methyl-2'-pyrrolinyl)-pyridine		315	3.82	247	4.2

TABLE 1 (Continued)

Substance	Formula	1st max.	log E	2nd max.	log E
5-Bromo-2-hydroxy-3-(1'-methyl-2'-pyrrolinyl)-pyridine		318	3.66	238	3.98

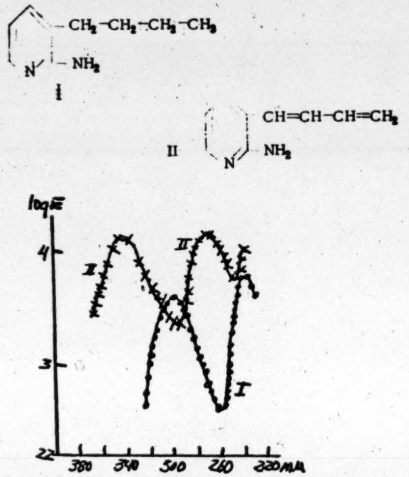


Fig. 3

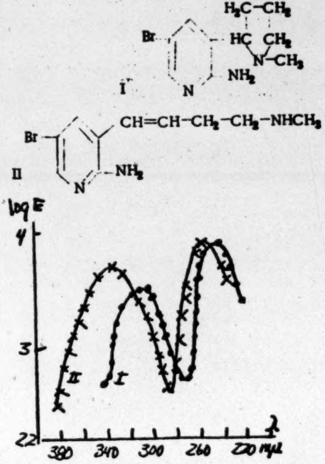


Fig. 4

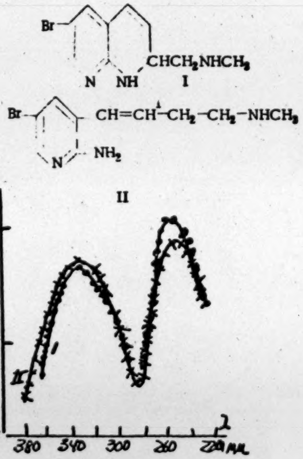


Fig. 5

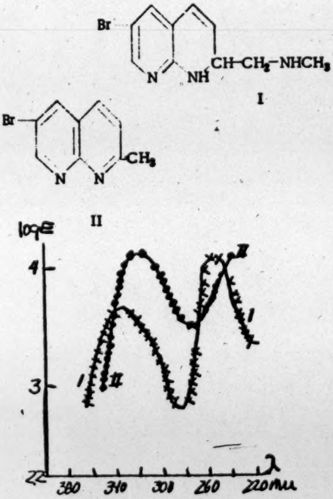
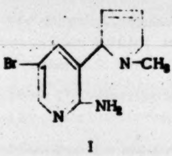
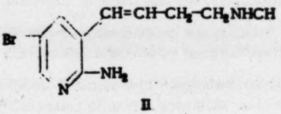


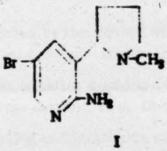
Fig. 6



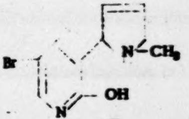
I



II



I



II

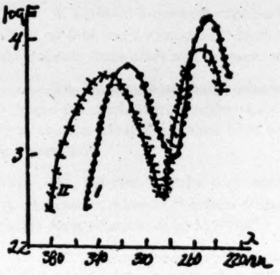


Fig. 7

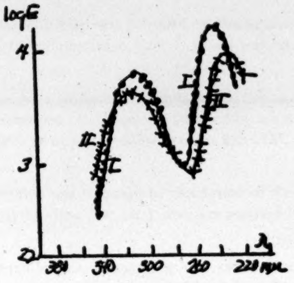


Fig. 8

A comparison of the absorption spectra of this base and of 5-bromo-2-aminometanicotine enabled us to make the necessary choice (Fig. 7).

The spectra of bases of type B should not differ significantly from that of 5-bromo-2-aminonicotine, since the position of the double bond of the side-chain is the same, and the ethylenimino-ring does not cause any shift in the position of absorption bands due to presence of double bonds in the molecule [5]. If, therefore, the base of m.p. 127-129° had structure B, its absorption curve should in its general contours conform with that of 5-bromo-2-aminometanicotine. This is not, however, found to be the case; the maxima of the absorption bands for the base of m.p. 127-129° are at 315 mμ (log E 3.82) and 247 mμ (log E 4.2), and for 5-bromo-2-aminometanicotine are at 335 mμ (log E 3.71) and 255 mμ (log E 3.92). A very similar absorption curve is found for the product of reaction of nitrous acid on the base of m.p. 127-129°, 5-bromo-2-hydroxy-3-(1'-methyl-2'-pyrrolinyl)-pyridine (Fig. 8).

The similarity of the absorption curves of the base and of 5-bromo-2-aminonicotirine should also be noted, as being in agreement with our views on the structure of the base of m.p. 127-129°, as a derivative of dihydronicotine of structure A, in which the double bond is not conjugated with those of the pyridine ring.

EXPERIMENTAL

1. 2-Aminonicotine was prepared by the method of Chichibabin and Kirsanov [6], and was purified by vacuum distillation followed by recrystallization from ethanol-acetone mixture; it melted at 124-124.5°.

2. 2-Amino-3-(4'-methylaminobut-1'-enyl)-pyridine (2-aminometanicotine) was prepared by the method of Goldfarb and Karaulova [7], m.p. 81-82° after vacuum distillation and recrystallization from heptane.

3. 2-Amino-3-(4'-methylaminobutyl)-pyridine (2-aminodihydrometanicotine) was obtained by hydrogenation of 2-aminometanicotine in presence of platinum catalyst. It was purified as the perchlorate, after regeneration from which it was recrystallized from heptane; m.p. 84-85°.

4. 2-Amino-3-(4'-dimethylaminobut-1'-enyl)-pyridine was prepared by the method of Goldfarb and Kondakova [8]. It was vacuum distilled, and converted into the picrate, from which it was regenerated and recrystallized from benzene; m.p. 85-86°.

5. 2-Amino-3-buta-1',3'-dienylpyridine was prepared by the method of Goldfarb and Kondakova [loc. cit.]. It was purified by steam distillation, and dried over calcium chloride; m.p. 74°.

6. 2-Amino-3-butylpyridine was prepared by hydrogenating 2-amino-3-buta-1',3'-dienylpyridine in presence of platinum catalyst, and was recrystallized from heptane; m.p. 46-47°.

7. 5-Bromo-2-aminonicotine was prepared according to Chichibabin and Kirsanov [6]. It was purified by vacuum distillation, followed by recrystallization from acetone; m.p. 138°.

8. 5-Bromo-2-amino-3-(4'-methylaminobut-1'-enyl)-pyridine (5-bromo-2-aminometanicotine) was obtained by the action of acetic anhydride on 5-bromo-2-aminonicotine [9], and was purified by vacuum distillation followed by recrystallization from heptane; m.p. 103-104°.

9. 6-Bromo-2-methylaminomethyl-1,2-dihydro-1,8-naphthiridine was prepared by the action of alcoholic alkali on 5-bromo-2-amino-3-(3'-bromo-4'-methylaminobut-1'-enyl)-pyridine [loc.cit.], and was recrystallized successively from ether and heptane; m.p. 155-156°.

10. 6-Bromo-2-methyl-1,8-naphthiridine was obtained by a Hoffmann degradation of the methiodide of 6-bromo-2-dimethylaminomethyl-1,2-dihydro-1,8-naphthiridine [loc.cit.], and was purified by recrystallization from aqueous ethanol and then from benzene. It changes into an opaque yellow mass at 213-215°, and melts at about 350°.

11. 5-Bromo-2-amino-3-(1'-methyl-2'-pyrrolinyl)-pyridine was prepared by the action of alcoholic alkali on 5-bromo-2-amino-3-(3'-bromo-4'-methylaminobut-1'-enyl)-pyridine [loc.cit.], and was purified by recrystallization from ethanol; m.p. 127-129°.

12. 5-Bromo-2-hydroxy-3-(1'-methyl-2'-pyrrolinyl)-pyridine was prepared by the action of nitrous acid on 5-bromo-2-amino-3-(1'-methyl-2'-pyrrolinyl)-pyridine [loc.cit.], and was recrystallized from benzene; m.p. 163° (decomposition).

The spectra were photographed with the aid of a Hilgers spectrograph, medium size model, dispersion in the region of 360 mμ 44mμ/mm, and of 250 mμ 12 mμ/mm. The source of light was an arc between tungsten electrodes. The plates were 13 x 18 cm, iso-ortho, sensitivity 400, developer metol-quinol, acid fixing bath. The spectra were measured by the method of equal blackening, and the beam of light was split by a Huefner quartz rhombus. The intensity of the standard beam of light was varied by means of a rotating sector. Places of equal blackening were found visually. The scale of wave lengths was calibrated by means of a copper arc. Each spectrum was repeated a number of times, and a result was taken to be satisfactory if a point on the last section of a spectrum lay on the curve given by the preceding section. The concentration of the solutions was varied by factors of 10 and 100.

We have pleasure in expressing our profound gratitude to E. V. Shpolsky for allowing us to execute the optical part of this research in the Optical Laboratory of which he is the head, and for his interest and assistance.

SUMMARY

1. A comparison of the ultra-violet absorption spectra of a series of substituted 2-aminopyridines, in which substituents of differing degrees of unsaturation are situated in position 3 of the ring, shows that the absorption maximum is shifted when the side-chain double bonds are in conjugation with those of the pyridine ring.

2. The results of the absorption spectra studies confirm the proposed structure of the compound obtained by the action of acetic anhydride on 5-bromo-2-aminonicotine.

3. Comparison of the absorption curves of the base of m.p. 127-129° obtained by the action of alkali on 5-bromo-2-amino-3-(3'-bromo-4'-methylaminobut-1'-enyl)-pyridine and of other systems allows the conclusion to be drawn that this base, m.p. 127-129°, is a derivative of dihydronicotirine.

Received February 23, 1952

Institute of Organic Chemistry
Academy of Sciences USSR
V. I. Lenin Pedagogic Institute

[1] O. N. Setkina, Ya. L. Danyushevsky, and Ya. L. Goldfarb, J. Gen. Chem., 18, 132 (1948)

[2] Ya. L. Goldfarb and M. S. Kondakova, Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 5, 610 (1951).

[3] M. L. Swain, A. Eisner, C. F. Woodward, B. C. Brice, J. Am. Chem. Soc., 71, 1341 (1949).

[4] Ya. L. Goldfarb and E. N. Karaulova, Proc. Acad. Sci. USSR, 65, 843 (1949).

[5] N. H. Cromwell, R. S. Johnson, J. Am. Chem. Soc., 65, 316 (1943).

[6] E. A. Chichibabin and A. V. Kirsanov, J. Russ. Chem. Soc., 56, 157 (1925); Ber, 57, 1163 (1926).

[7] Ya. L. Goldfarb and E. N. Karaulova, J. Gen. Chem., 18, 117 (1948).

[8] Ya. L. Goldfarb and M. S. Kondakova, Proc. Acad. Sci., USSR, 55, 619 (1947).

[9] Ya. L. Goldfarb and M. S. Kondakova, Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 5, 660 (1951).

BLANK
PAGE

CHEMICAL TRANSFORMATIONS OF CELLULOSE MACROMOLECULES CAUSED BY OXIDANTS

PART 7. CHEMICAL TRANSFORMATIONS OF CELLULOSE DUE TO ITS OXIDATION WITH SODIUM HYPOCHLORITE

E. D. Kaverzneva, V. I. Ivanov, and A. S. Salova

Calcium hypochlorite and chlorine are the most widely used oxidants for the bleaching of cellulose materials. The careful use of these oxidants, under the appropriate conditions, makes the fibers whiter, without significantly affecting their strength and chemical stability, but deviation from these conditions readily leads to severe damage of the fibers. On the other hand, a number of industrial processes require a definite lowering of the viscosity of cellulose solutions, or modification of its physical and chemical properties (production of viscose, lacquers, oxycelluloses). It is not therefore surprising that numerous researches have been undertaken with the object of elucidating the changes produced in the properties of cellulose fibers by chlorine and hypochlorite. The general conclusion which emerged from these researches was that chlorine and the hypochlorite ion belong to the category of non-specific oxidants, which react with various parts of the cellulose macromolecule to produce, according to the reaction of the solution, either the "reducing" type of oxycellulose or the "acid" type [1].

All chemical studies of oxycelluloses were of a largely descriptive nature until well into the forties of this century. However, the past ten years have seen the elaboration of precise methods for the determination of the various functional groups of oxycelluloses, even when present in only minute amount in the macromolecule. Thus the analytical techniques applied and developed in our laboratories allow of the determination of total and "uronic" carboxylic groups with an accuracy of up to 0.05% of the weight of the sample, of aldehyde groups with an accuracy of up to 0.02%, and of carbonyl groups with an accuracy of up to 0.1%. These analytical advances make it possible to undertake a more profound study of the chemical processes taking place during the oxidation of cellulose by non-specific oxidants.

The chemical changes produced by such oxidants as chlorine, hypochlorite ion, perhydrol, atmospheric oxygen in alkaline media, and ultra-violet irradiation, and also the effect of pH changes on these processes, have not yet received any detailed study. Moreover, there are many mistaken beliefs current in this field. Thus Jurisch [2] says that perhydrol acts only on hydrate-cellulose, and only at concentrations of alkali greater than 8%. It appears from our work that chemical changes are observed in cellulose after the action of perhydrol at all pH values. The view has gained acceptance, on the basis of the work of Unruh and Kenyon [3], that nitrogen peroxide is a strictly specific oxidant of primary hydroxy groups, whereas we have found [4] that the activity of this oxidant is not so selective.

The object of the present research is to study the chemical processes taking place when hypochlorite, the most widely used oxidant, acts on cellulose. A peculiarity of hypochlorite is that the oxidant varies according to the pH of the medium; free chlorine predominates in acid solutions, and the concentration of undissociated hypochlorous acid rises as the reaction approaches neutrality, while with further rise in pH the concentration of hypochlorite ion rises [5]. The stability of HOCl is at a minimum at pH 6.7, and the maximum at pH 13 (Fig. 1).

Oxidation of monosaccharides by chlorine in acid solutions involves oxidation of the aldehyde group, as well as primary and secondary hydroxy groups, with subsequent fission of the carbon chain [6]. The primary hydroxyl of polyhydric alcohols appears to be the first to be oxidized [7].

The mechanism of oxidation of carbohydrates by halogens must be regarded as being far from being elucidated, although the work of Shilov and Yasnikov [8] is a valuable contribution thereto.

The present paper describes the results obtained for oxidation of purified cotton cellulose (0.05 N NaClO; 18-22°; modulus 1:20), at different pH of the solutions, uptake of oxygen being the same in all experiments.

Oxidation was limited to use of 5-15 atoms of oxygen per 100 glucose residues, since when more oxygen is used the process is complicated by superimposition of secondary processes. Only for the study of certain special problems was more profound oxidation applied, using up to 200 atoms of oxygen per 100 glucose residues, in acid and alkaline solutions. In addition to this, all analyses were repeated for a number of preparations after additional oxidation of aldehyde groups with sodium hypoiodite in alkaline solution (pH 9.2).

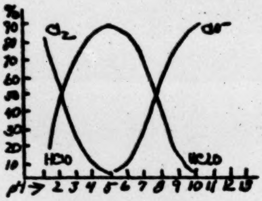


Fig. 1. Changes in the relations $Cl_2 \rightleftarrows HClO \rightleftarrows ClO^{\prime}$ at different pH values of the solution.

EXPERIMENTAL

Pre-treatment of cotton. The cotton was treated with 1% NaOH for 10 hrs at 100°, washed, dried, and extracted with dichloroethane and 1:1 methanol-ether mixture. Before taking it for the oxidation experiments the cotton was again washed with warm 1% $NaHCO_3$ solution and with water. Analysis gave the following: ash content 0.19%; total COOH groups 0.04%, uronic acid COOH 0.07%; CHO 0.072%; iodine number 0.49; N 0.02%; viscosity of 0.2% solution 840 millipoise.

Oxidation. The NaClO solutions were prepared by saturation of cold 10% NaOH with chlorine. The NaOH concentration of a sample of the solution was determined separately, after decomposing hypochlorite with H_2O_2, and the rest of the solution was made neutral by adding the calculated amount of hydrochloric acid. An equal volume of buffer solution was added to this basic solution, for the oxidation experiments, which were conducted with 0.049 N-NaClO at pH 4.6, 6.8, and 11. The modulus was 1:20 at 16-25°; the time needed for consumption of the scheduled amount of oxygen was derived from the difference between the active chlorine content of the experimental and of control solutions, at various times. The oxidized samples were then washed with a weak solution of $NaHSO_3$ and with water, demineralized in 0.5% acetic acid, and repeatedly washed with water. They were then allowed to dry, and were further dried at 50° before being analyzed.

Determination of total COOH-group content, from the reaction $COOH + CH_3COOCa = RCOOCa + CH_3COOH$ [9]. Portions (0.2-1.0 g) of oxycellulose were allowed to react for 24 hrs at room temperature with 0.5 N calcium acetate, prepared with CO_2-free distilled water, and of pH 7.2-7.5. The free acetic acid formed was titrated with 0.02 N NaOH, to pH 8.3 (phenolphthalein indicator). The difference between the result of this titration and of a blank titration gave the carboxy group content. Determination of uronic COOH-groups from the reaction $CHO-(CHOH)_4COOH + HCl \longrightarrow C_5H_4O_2 + 3H_2O + CO_2$. This was performed as a micro-variant of the decarboxylation method, using 12% HCl [10]; CO_2 was absorbed in 0.02 N-$Ba(OH)_2$, excess of which was titrated with 0.02 N-HCl.

Determination of aldehyde groups, from the reaction $RCHO + NaOI = RCOOH + NaI$ [11]. A portion of oxycellulose (0.2-0.5 g) was treated with 20 ml of ~0.03 N iodine solution + 10 ml of 0.05 M-$Na_2B_4O_7$ (pH 9.2) for 2 hrs at 25°, after which 30 ml of 0.1 N-HCl was added, and the solution was titrated with 0.01 N-$Na_2S_2O_3$; a control titration was done at the same time.

Determination of total carbonyl groups from the reaction $RCOR' + NH_2OH \cdot HCl = RR'CNOH + H_2O + HCl$ [12]. After carboxyl groups had been neutralized with calcium acetate the cotton was washed with water, and dried, and a 1.0 g sample was treated with a freshly prepared 2.5% NH_2OH solution [200 ml of solution contain 5 g of $NH_2OH \cdot HCl$ and 20 ml of 0.5N-NaOH (pH ~5)]; for 2 hrs at room temperature. The solution is titrated with 0.1 N HCl, with bromophenol blue indicator, taking the color change from blue to yellowish-green as the end-point (pH 3.2); a blank titration is performed at the same time. The method was checked by determining total nitrogen in the preparations after condensation with NH_2OH. These analyses regularly gave a smaller amount of nitrogen than would correspond with that found by titration of the amount of CO-groups; the reason for this discrepancy was not discovered. The Tables give the content of total carbonyl groups (and of keto-groups, as the difference from aldehyde groups), in accordance with the determinations of nitrogen.

Viscosity was determined in 0.2% solutions of oxycellulose in cuprammonium reagent (NH_3 20%, Cu 1.5%), and in some cases for acetone solutions of nitrate esters. Additional oxidation of aldehyde groups with NaOI was performed under the same conditions as for their determination, but allowing more time. The results are given in Table 1.

The following conclusions emerge from these analytical data:

1. The following changes take place in the initial stages of oxidation of the macromolecule of oxycellulose by sodium hypochlorite in weakly acid solution (pH 4.6):

(a) gradual rise in the COOH-group content;
(b) gradual rise in aldehyde group content;
(c) appearance of keto-groups;
(d) the number of uronic acid carboxylic groups exceeds that of total COOH-groups.

2. The chemical changes due to oxidation in neutral solution (pH 6.8) are of the same order as in acid solutions, but the process proceeds much more rapidly than in the latter. The number of uronic acid carboxylic groups is greater than that of free COOH-groups.

3. The following is observed during oxidation in alkaline solutions (pH 11):

(a) a more abrupt rise in total COOH-group content, in relation to bound oxygen, than in acid solutions;
(b) almost complete absence of aldehyde groups (except in the case of deep oxidation);
(c) formation of ketonic groups;
(d) the number of uronic carboxylic groups is much smaller than the total number of COOH-groups.

These conclusions are shown graphically by the curves of Figs. 2 and 3.

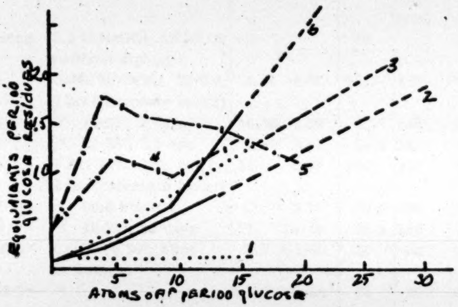
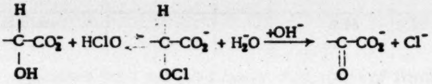


Fig. 2. Increase in functional group contents in oxycellulose as oxidation proceeds; 1) CHO, pH 11.0;2) COOH, pH 4.6; 3) CHO, pH 4.6; 4) CO, pH 11.0; 5) CO, pH 4.6; 6) COOH, pH 11.0.

During equal intervals of time the curve representing binding of oxygen by cellulose lies much higher for neutral solutions than for acid or alkaline ones; this effect was taken to signify that the chief oxidant in the system $Cl_2 \rightleftharpoons HClO \rightleftharpoons ClO'$ is undissociated hypochlorous acid [13].

Yasnikov and Shilov [8] advance a different view, according to which HClO first gives an ester with a hydroxy group, and this ester then eliminates HCl, giving a carbonyl group:



$$-\overset{H}{\underset{OH}{C}}-CO_2^- + HClO \rightleftharpoons -\overset{H}{\underset{OCl}{C}}-CO_2^- + H_2O \xrightarrow{+OH^-} -\underset{\underset{O}{\|}}{C}-CO_2^- + Cl^-$$

This mechanism cannot be regarded as being proven, although there do exist arguments in its favor.

Position of the carboxylic groups in the glucose residues of the cellulose macromolecules

It follows from a study of Table 1 that with oxidation in acid or neutral solutions the number of "uronic" COOH-groups exceeds that of free carboxylic groups. We have explained this [14,15] as being due to presence of traces of carbonate esters, and to formation of lactones from part of the uronic COOH-groups of these oxycelluloses. Since we have as yet no accurate way of estimating the extent of such lactone formation, the determination of non-uronic COOH-groups in these products is difficult.

Oxidation of the primary OH-group at C_6 to COOH is evident in the products of alkaline oxidation, as well as accumulation of non-uronic COOH-groups. It may be supposed that some of these will be at the end of chains, but it follows from calculation of the number of non-uronic COOH-groups per macromolecule of oxycellulose

TABLE 1

Analysis of oxycelluloses. (All values for functional groups are given as equivalents per 100 glucose residues).

No. of preparations	Conditions of oxidation	pH of reaction solution	No. of atoms of O bound (from amount of NaOCl used)	Yield of oxycellulose, %	Degree of polymerization	COOH-groups			Carbonate groups	Aldehyde groups	Carbonyl groups (total), from cellulose oxime nitrogen	"Ketonic groups
						total (by the Ca acetate method)	"uronic"	non-uronic (by difference)				
4	0.049 N NaOCl, 19-22°, 7 hrs (acetate buffer) 1:20	4.6	4.25	~100	500	0.26	0.26	Nil	–	0.32	2.14	1.82
1	" 57 hrs	4.6	7.09	~97.2	390	0.425	0.76	?	–	0.58	2.20	1.52
7	" 14 days	4.6	13.16	95.7	220	0.74	1.04	?	0.22	1.02	2.47	1.45
Prep. b-z	0.13 N NaOCl, 24 hrs., 17°	~5	20.2	92	–	0.57	1.10	?	–	0.98	1.96	0.98
1-deep	0.23 N NaOCl, 25°, 24 hrs	~3.1	44.6	~84	114 (nitrate)	1.66	1.91	?	0.17	1.68	2.17	0.49
2-deep	0.2 N NaOCl, 22°, 24 hrs (without drying)	~1	–	~48	–	2.95	3.82	?	–	2.14	3.71	1.57
5	0.049 N NaOCl, 22-25°, 2 hrs (phosphate buffer)	6.86	4.96	100	475	0.25	0.33	?	–	0.32	1.55	1.23
8	" 19-20°, 5 days	6.86	7.59	96.6	245	0.61	0.83	?	–	0.49	1.73	1.24
2	" 22-28°, 7.5 hrs.	6.86	9.11	96.8	342	0.76	1.01	?	0.09	0.53	1.63	1.10
6	0.049 N NaOCl. 20°, 6 hrs.(carbonate buffer)	11	4.96	100	420	0.38	0.43	?	–	0.16	1.26	1.10
3	" 56.5 hrs. 20°	"	9.11	98.6	390	0.65	0.57	0.08	0.0	0.16	1.09	0.93
9	" 19-20°, 20 days	11	14.38	95.9	180	1.47	0.71	0.76	0.0	0.17	1.50	1.33
TsB-3*	$Ca(OCl)_2$, 20°, 4 hrs in 2 stages	9.5	Given 100-160	85	64	3.49	1.58	1.91	–	1.73	3.81	2.08
TsB-1*	"	9.5	Given 200-230	75	32	4.32	3.06	1.26	–	1.33	5.11	3.78
Prep.B	0.094 N NaOCl, 1:20, 24°, 3 days (borate buffer)	9	–	98.4	–	1.44	0.83	0.61	–	0.20	1.57	1.37
	Initial cellulose					0.15	0.25	?	0.025	0.20	0.51	0.31

---

* We obtained the preparations TsB-1 and TsB-3 from F. P. Komarov of TsNIIB, for which we thank him.

that it must be greater than one. It follows that formation of some of the COOH-groups is associated with opening of the pyranose rings of the glucose residues.

Carbonic acid esters are present in the products of oxidation in acid and neutral solutions, but their number is small, and does not rise as depth of oxidation increases. They are apparently decomposed as formed, with breakdown of the cellulose chain.

Position of aldehyde groups in the glucose residues of the cellulose chain

In order to ascertain the position of the aldehydic groups in the glucose residues they were oxidized to carboxylic groups under specific conditions, with the object of finding whether uronic or non-uronic acids are

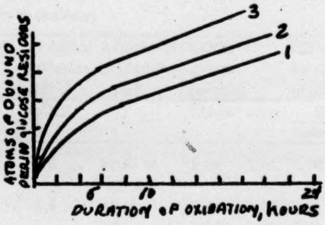
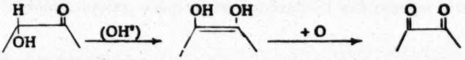


Fig. 3. Oxygen used for oxidation of cellulose at various pH: 1) pH 11.0; 2) pH 4.6; 3) pH 6.8

produced. The products of selective oxidation of aldehydic groups with NaOI at pH 9.2 were washed and demineralized, and were analyzed for all their functional groups. This treatment should in theory lead to increase in the content of total free carboxylic groups, by an amount equivalent to diminution in the content of aldehydic groups. Should these aldehyde groups have been located at carbon atom 6 of the glucose residues the content of uronic carboxylic groups should also rise. The results of these experiments are given in Table 2.

It is, however, difficult to draw firm conclusions from these experiments, since during oxidation in alkaline solutions considerable dissolution of the oxycelluloses produced takes place, the more oxidized units of the chains having a stronger tendency to pass into solution. This leads to a lowering of the carboxylic group content of the residue, making it impossible to draw up a balance of functional groups. This effect is particularly evident for highly oxidized preparations in acid solution (Nos. 7-9). It appears from a consideration of the data for low degrees of oxidation (experiments Nos 1, 2, 3, and 4), and for deep oxidation in alkaline solution (Nos. 5 and 6), that the content of uronic carboxylic groups rises after oxidation of aldehydic groups, suggesting that some of these groups must be at position 6 of the glucose residues.

A conclusion of this sort could not be made for the products of deep oxidation of cellulose in acid solution, since the number of uronic carboxylic acid groups falls abruptly, owing to the solubility of these products. At first sight it is hard to understand the reason for the rise in the number of ketonic groups after oxidation of aldehydic groups, which appears to be a regular feature of products of deep oxidation (Nos. 5-9). We have suspected that during oxidation with sodium hypoiodite in weakly alkaline solution hydroxyketone groupings can undergo oxidation, in addition to aldehydic groups, after conversion into endiol groupings.



This reaction could lead to increase in the number of ketonic groups without formation of new carboxylic groups.

However, as was shown in our previous publication [15], the hydroxy-ketone grouping of oxycelluloses does not undergo conversion into endiol at pH$<$10, and is not oxidized by hypoiodite. For this reason a different explanation of the apparent rise in ketonic groups must be sought, and this may be found in formation of lactones of newly formed carboxylic groups; the lactone reacts with hydroxylamine instead of the oxidized aldehyde group. This gives the appearance of a rise in ketonic group content. The nitrogen content of the cellulose oximes obtained before and after oxidation of aldehydic groups was about the same, in accordance with this supposition; aldoxime nitrogen is replaced by an equivalent amount of hydroxamic acid nitrogen.

The basic conclusion to be drawn from these experiments is that some of the aldehyde groups of the oxycelluloses obtained by both acid and alkaline oxidation are at position 6 of the glucose residue. The number of aldehydic groups in this position is much smaller after alkaline than after acid oxidation. The number of other aldehyde groups greatly exceeds one per oxycellulose macromolecule.

Attempt at formulating a scheme of oxidation processes associated with the action of sodium hypochlorite on cellulose

Our experiments have led us to the conclusion that oxidation of cellulose with sodium hypochlorite involves formation not only of carboxylic and aldehydic groups, as has been shown by numerous authors, but also of α-hydroxyketone groupings, carbonate groupings, and lactone bonds. The velocity of simultaneously proceeding oxidation processes depends on the pH of the solution, and they lead to production of oxycelluloses of differing chemical properties.

TABLE 2

Analyses of oxycelluloses before and after additional oxidation of aldehydic groups (as equivalents per 100 glucose residues)

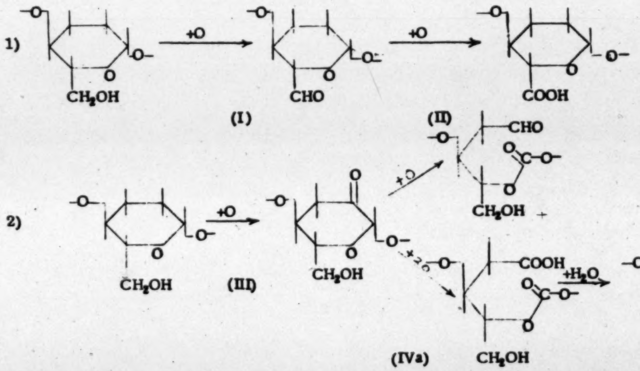
Expt. No.	pH during oxidation with NaOCl	Additional oxidation with	COOH-groups (uronic)		CO + COH by titration of liberated HCl		CHO		CO (by difference)		CHO at C_6	Total oxime N	
			before	after	before	after	before	after	before	after		before	after
1	4.6	NaIO at pH 9.2	1.04	1.51	2.98	1.91	0.38	Nil	2.0	1.91	0.47		1.56
2	4.6	ditto	1.04	1.39	3.01	1.97	1.0	"	2.02	1.97	0.35		
3	5	"	1.10	1.32	3.01	1.85	0.98	"	2.03	1.85	0.22	1.33	1.28
4	9.0	"	0.83	0.83	2.49	2.43	0.20	0.035	2.29	2.39	0		1.53
5	9.5	"	3.06	3.38	5.39	5.95	1.33	–	4.05	5.95	0.32	6.02	5.61
6	9.5	"	1.58	1.91	4.34	4.74	1.73	–	2.61	4.74	0.32	3.99	–
7	3.1	ClO_2 in acid solution	1.91	1.13	2.38	3.7	1.21	0.05	1.20	3.64			
8	3.1	NaIO at pH 9.2	1.91	1.18	2.38	3.65	1.39	Nil	0.99	3.65		2.08	1.71
9	1	ditto	3.74	1.69	6.20	5.97	2.14	–	4.06	5.97		3.59	

Two parallel reactions proceed simultaneously in acid solutions:

(1) oxidation of primary OH-groups at C_6, to give aldehydes, which are further oxidized to carboxylic groups;

(2) formation of α-hydroxyketones, which are further oxidized with opening of the ring, and formation of carbonic acid esters.

Oxidation in acid solutions; pH 3-5:

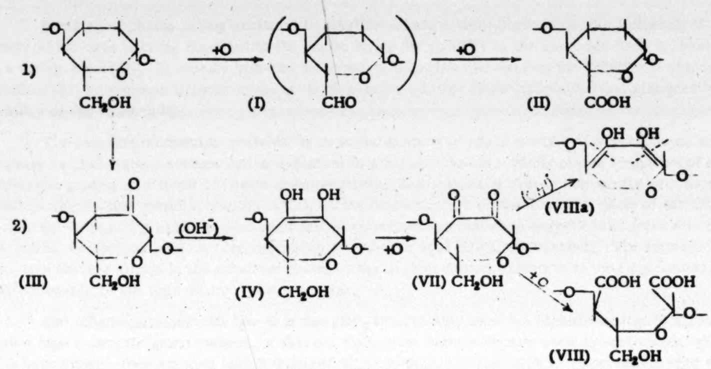


The oxycellulose formed has reducing properties (C_1 and C_6 aldehyde groups, α-hydroxyketone groups), and is readily depolymerized in alkaline solution, owing to hydrolysis of carbonic acid ester residues in the chain, and to enolization of aldehydic and ketonic groups [16]. Additional oxidation of aldehydic groups leads to increase in the number of uronic carboxyls, at the expense of those aldehydic groups which are at position 6. Not all the carboxylic groups are free ones, some of them being included in lactone rings, as a result of which direct determination of acidity does not reveal all of them.

Oxidation processes in neutral solution are analogous to those in acid solution. In alkaline solutions the same two reactions (formation of aldehydes and ketones) initiate the process, which then develops differently. Stage I proceeds very quickly, and C_6 aldehydic groups do not accumulate, but are rapidly further oxidized to uronic carboxylic groups (II).

In the second reaction the monoketone (III) formed isomerizes to the endiol (VI), which is rapidly oxidized to the diketone (VII), followed by opening of the ring, with formation of two carboxylic groups, giving a compound with a shorter carbon chain (VIII).

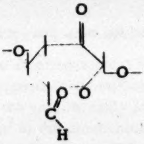
Oxidation in alkaline solution; pH 11.



There are no carbonic acid esters, and only a very few aldehydic groups, in oxycellulose obtained in alkaline solution. The esters, if formed, undergo hydrolysis in alkaline solution, and aldehydes are rapidly oxidized to carboxylic groups. On the other hand, there is a high content of non-uronic carboxylic groups formed by opening of the pyranose ring at points of inclusion of keto- and diketo-groups.

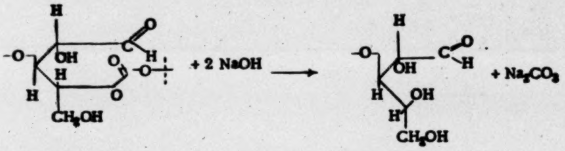
There are initially no lactone groups present in oxycellulose formed in alkaline solution, but these groups are formed during acid treatment of the products for their demineralization.

The reaction mechanisms given include only the simpler, partly experimentally confirmed, transformations of glucose residues of the cellulose macromolecule. There can be no doubt that oxidation of primary OH-groups at C_6 and of secondary groups at C_2 (or C_3) may take place in the same glucose unit.



In such cases a large number of different decomposition products should be formed, and an indication that the reaction may proceed in this way is afforded by the fact that our experiments on condensation with NH_2OH gave only negligible amounts of glucosamine, with larger amounts of some as yet unidentified nitrogen-containing products [15].

The fall in the degree of polymerization found in acid oxidation media is not connected with presence of aldehydic groups, as is shown by the stability under these conditions of dialdehyde-cellulose. Hydrolytic decomposition in acid solutions is accelerated owing to hydrolysis of carbonic acid esters, the amount of which does not rise with progressive increase in depth of oxidation. This indicates that they are decomposed as they are formed.



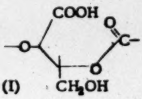
Apart from this, the stability of glucoside bonds in acid solutions is lowered when carboxylic groups are formed [17,3].

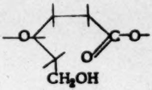
Breaking of chains during oxidation in alkaline solutions takes place under the influence of aldehydic groups which have become modified to the enolic form; the stability of the glucoside bond is lowered by proximity to a double bond [18]. It appears from the more recent experimental data on the stability of glucosides in alkaline solutions that keto-groups situated at the α- or β-position relative to the glucoside bond also greatly reduce the stability of the latter [19].

The reaction mechanism proposed by us explains many of the properties of oxycelluloses, such as rapid increase in COOH-group content during oxidation in alkaline solution, chiefly due to formation of non-uronic carboxylic groups, as a result of fission at keto-carbons. Our scheme is also in conformity with those structural features which cause excess evolution of CO_2 during determination of uronic acids (esters of carbonic acid, lactones). It logically explains the abrupt fall in viscosity observed when oxycelluloses from acid oxidation are placed in alkaline solution (decomposition of carbonic acid esters, enolization). The impossibility of accumulating ketonic groups in the cellulose chain, owing to their further oxidation as they are formed, is also understandable in the light of our reaction scheme.

Our scheme also explains how it is that HIO_4 in acid solution gives high-molecular "dialdehyde-celluloses" with a high aldehydic group content, or that dry N_2O_4 gives high-molecular carboxyl-celluloses, while treatment with hypochlorite does not give highly oxidized high-molecular oxycelluloses. Hypochlorite-type oxidation is associated with formation of functional groups, some of which cause degradation of the chain in acid and neutral solutions, and others give this effect in alkaline solution. It is thus not possible to provide conditions such that the oxycellulose chain would be stable, and to this is due the non-specificity of hypochlorite as an oxidant.

Staudinger and Sohn [20], who in 1939-1940 proposed a scheme for the oxidative degradation of cellulose, attributed the instability of the products to the action of alkalis to formation in the chain of modified glucose residues of the type of carbonic acid ethers (I) and esters (II).


(I)

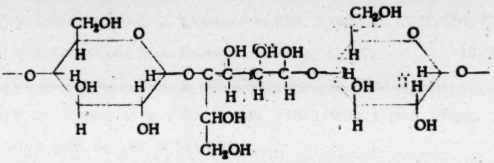

(II)

Both schemes were purely speculative, and were not backed by any experimental evidence whatsoever.

Schulz [21] in 1947 tried to provide an experimental basis for Staudinger's scheme, consisting of reaction velocity measurements. Finally, Heuser suggests in his monograph [22] a variant of Staudinger's scheme, also without any experimental basis. Nor does the very recently published paper of Haskins and Hogsed [23] make any real contribution; they suggest a variant of the mechanism already considered by us, depending on weakening of the glucoside bond by enolization of aldehydic groups [18]. We thus see that up to now no reaction schemes having any experimental basis whatsoever have been advanced for the oxidation of cellulose by non-specific oxidants.

Our paper represents the first attempt at providing such a scheme, based on chemical evidence. Some of the assumptions made earlier have been confirmed by our findings; in particular, the presence of carbonic acid ethers (esters) has been demonstrated with certainty in celluloses oxidized in acid solution, although in very small amount. We have also demonstrated the presence of the hydroxyketonic grouping. Presence of diketones is very probable, although we have no direct evidence for this. Finally, our results have shown the presence in oxycelluloses of ester groups other than carbonate ones; the ease of their formation in acid solution and of their hydrolysis in alkaline solution incline us to believe that we here have to do with lactone formation in separate glucose units, similarly to lactone formation in low molecular weight hydroxy-acids.

We were not able to establish presence of ester type bonds, as proposed by Staudinger and Heuser, since the reaction of formation of hydroxamic acids tells us nothing of the location of the ether groups. Our observation that such groups are formed secondarily when oxycelluloses are treated with aqueous acids cannot be made compatible with Staudinger's ester theory. The formation chiefly of uronic carboxylic groups in the initial stages of oxidation is an additional argument against oxidation of carbon atom 1, since this should lead to formation of non-uronic COOH-groups. The possibility of oxidation at C_1 cannot, however, be entirely excluded, especially if we take into account Strepikheev's views [24] as to the possible presence in the cellulose chain of non-cyclic glucose residues:



There are many other details of the oxidative process for which we are not at the moment able to give unambiguous explanations. We regard the mechanism advanced by us as being only a first approximation in accordance with the experimental material obtained by us for reactions of oxidation of cellulose.

SUMMARY

1. Chemical changes in the structure of cotton cellulose due to oxidation with sodium hypochlorite at different pH have been investigated by means of specific quantitative micromethods.

2. The following groups have been found in the oxycelluloses obtained by hypochlorite oxidation: uronic and non-uronic carboxylic groups, C_6 aldehydic groups, α-hydroxyketonic and lactone groups, and carbonic acid ester (ether) groupings.

3. The oxycelluloses obtained by oxidation in acid and neutral solution have a similar structure, different from that obtained in alkaline solution.

4. A reaction mechanism is advanced for the oxidative degradation of cellulose by the action of sodium hypochlorite at various pH. This mechanism satisfactorily explains the chemical behavior of the oxidation products.

5. The various oxidative processes shown to occur may be utilized for the better control of such processes, and for the preparation of cellulose oxidation products of known properties.

Received April 2, 1951

Institute of Organic Chemistry
Academy of Sciences USSR

LITERATURE CITED

[1] A. Nastyukov. Ber. 33, 2238 (1900); 34, 719 (1901); A. Nastyukov, O. Golova, and A. Kolli, Ber. 60, 2591 (1928); C. Birtwell, D. Clibbens, B. Ridge, J. Text. Inst. 16, 13 (1925).

[2] I. Jurisch, Ang. Chem. 54, 305 (1941).

[3] C. Unruh and W. Kenyon, J. Am. Chem. Soc. 64, 127 (1942).

[4] E. D. Kaverzneva. Proc. Acad. Sci. U.S.S.R., 68, 865 (1949).

[5] B. Ridge, A. Little, J. Text. Inst. 33, 133 (1942).

[6] H. Hlasewitz, Ann. 119, 281 (1861); 155, 120 (1870); H. Kiliani, Ber. 21, 3276 (1888); Ann. 182 (1861); H. Isbell, W. Pigman, J. Res. Natl. Bur. St. 10, 337 (1933).

[7] E. Fischer, Tafel, Ber., 20, 3384; 22, 106 (1889).

[8] E. A. Shilov and A. A. Yasnikov, Textile Industr. No. 11, 34 (1950).

[9] B. Meesook, C. B. Purves, Paper Trade J., 123, 223 (1946).

[10] A. S. Salova, J. Anal. Chem., 4, 354 (1949).

[11] A. Martin, D. Smith, M. Harris, J. Res. Natl. Bur. St., 27, 449 (1941).

[12] E. K. Gladding, C. B. Purves, Paper Trade J., 116, 26 (1943).

[13] F. Forster, F. Jorre, J. prak. Chem., 59, 53 (1898); 63, 147 (1901).

[14] E. D. Kaverzneva, Proc. Acad. Sci. U.S.S.R., 68, 5 (1949).

[15] E. D. Kaverzneva and A. S. Salova, Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 6, 804 (1951).

[16] E. D. Kaverzneva, Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 6, 800 (1951).

[17] V. I. Ivanov and E. D. Kaverzneva, Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 5, 498 (1945).

[18] V. I. Ivanov and E. D. Kaverzneva, Prog. Chem. 13, 281 (1944).

[19] Cl. Ballou, K. P. Link, J. Am. Chem. Soc., 72, 3147 (1951).

[20] E. Staudinger, A. W. Sohn, Ber., 72, 1709 (1939); J. prak. Chem. [2] 155, 177 (1940).

[21] G. Schulz, Ber., 80, 335 (1947).

[22] E. Heuser, Chemistry of Cellulose, 1944.

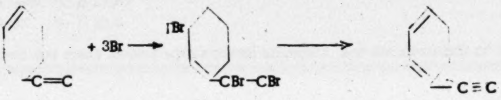
[23] J. F. Haskins, M. J. Hogsed, J. org. Chem., 15, N.6, 1264 (1950).

[24] A. A. Strepikheteev, Proc. Acad. Sci. U.S.S.R., 67, 471 (1950)

1-ETHINYLCYCLOHEXA-1,3-DIENE AND ITS DERIVATIVES

A. D. Petrov and A. V. Kulikova

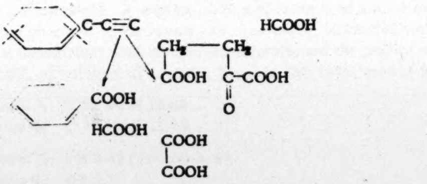
We took as the starting material for the synthesis of this new-acetylenyl hydrocarbon 1-vinylcyclohex-3-ene, which is readily available. The acetylenic hydrocarbon could not be obtained by successive chlorination and dechlorination of the vinyl hydrocarbon, but bromination at −2° to +2°, giving the tribromide, followed by debromination gave the required product. The record of bromination of vinylcyclohexene by Lebedev [1], and the results of our study of the product obtained allow us to assume that the reaction proceeds as follows:

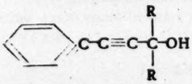


(I)

A molecule of bromine first adds on the double bond of the side-chain, and an atom of bromine enters the ring according to the mechanism of Tishchenko [2], with displacement of the double bond to the α-position. We at first oxidized hydrocarbon (I) under the conditions recommended by Lebedev [3] for oxidation of vinyl-cyclohexene, but we obtained only benzoic acid.

It is evident that 1-ethinylcyclohexa-1,3-diene, being a derivative of dihydrobenzene, does not undergo fission at the double bonds when treated with chromic acid mixture, but undergoes further dehydrogenation of the ring. We next tried oxidation with 0.5% potassium permanganate, whereby we obtained cyclohexa-1,3-diene-1-carboxylic acid and ketoglutaric acid, suggesting that oxidation proceeds as follows:



The presence of a triple bond in hydrocarbon (I) was confirmed by its hydration, which gave 1-acetyl-cyclohexa-1,3-diene, identified as its 2,4-dinitrophenylhydrazone, m.p. 230° [that the hydrocarbon (I) is not phenylacetylene is shown by the fact that the dinitrophenylhydrazone of acetophenone melts at 249°] The hydrocarbon (I) gave the corresponding tertiary acetylenic alcohols, by a Grignard reaction with diisopropyl ketone or benzophenone. These alcohols, similarly to Malenok's tertiary alcohols [4] (of the type  , i.e., with phenyl radicals), are characterized by their great stability, in distinction to acetylenic alcohols with conjugated multiple bonds in aliphatic radicals. They do not polymerize when stored for eight months.

EXPERIMENTAL

Several kilograms of 1-vinylcyclohex-3-ene was obtained by heating divinyl in a steel autoclave for 6-8 hrs at 140-160°/50 atm. It had b.p. 49-51°/50 mm, d_4^{20} 0.8299; n_D^{20} 1.4647; found MR_D 35.96; calculated MR_D 36.03.

Bromination was conducted to the tribromide, the amount of bromine adding on being derived from the gain in weight of the flask with the product. The tribromide is a dark, slightly fuming liquid, with an acrid odor. It was debrominated by heating under reflux on a water bath with 20% alcoholic potassium hydroxide, which was added in small portions, each addition being followed by considerable evolution of heat. After completion of the reaction the potassium bromide formed was filtered off, the alcohol was distilled off from the filtrate, the residue was diluted with water, and the solution was extracted with ether. The extract was fractionally distilled, giving a fraction of b.p. 52-54°/49 mm, d_4^{20} 0.8489; n_D^{20} 1.4865; found MR_D 35.15; calculated MR_D 33.94, yield 20% of the 1-vinylcyclohex-3-ene taken.

Oxidation of the fraction of b.p. 52-54°/49 mm. 1 g of potassium permanganate was added to an emulsion of 4 g of the hydrocarbon in 200 ml of water; the reaction proceeded energetically, and the solution was rapidly decolorized, 24 g of permanganate being added altogether. The products included acids only, and after acidification crystals of 2,3-dihydrobenzoic acid (cyclohexa-1,3-diene-1-carboxylic acid), m.p. 93.5-94° [5]*. This acid has a tendency towards conversion into benzoic acid when boiled with water, during recrystallization. Its amide melts at 105°.

Found in amide of m.p. 105° %: N 11.87
Calculated for C_7H_9ON %: N 11.3

The filtrate from this acid was made neutral with aqueous ammonia, and the silver salt of α-ketoglutaric acid was precipitated from it.

Found %: C 15.93; H 1.64; Ag 59.5
$C_5H_4O_5Ag_2$. Calculated %: C 16.6 ; H 1.10; Ag 59.9

Hydration of the hydrocarbon (I) gave a ketone, the 2,4-dinitrophenylhydrazone of which melted at 230-231°:

Found %: N 19.01
$C_{14}H_{14}N_4O_4$. Calculated %: N 18.65

Synthesis of 1-(cyclohex-1',3'dienyl)-4-methyl-3-isopropylpent-1-yn-3-ol

1-Ethinylcyclohexa-1,3-diene (24 g) was added in small portions to a solution in 150 ml of ether of 3.7 g of Mg and 16.4 g of C_2H_5Br. The reaction proceeded energetically, with evolution of gas, and the mixture was then heated for 3 hrs, and left overnight. A solution of 18 g of diisopropyl ketone in ether was then added; the reaction, which commenced after half of the ketone had been added, proceeded violently, and required constant cooling. The complex was decomposed with ammonium chloride, and the product was fractionated, giving 9.2 g of a fraction of b.p. 162-164°, n_D^{20} 1.5030; d_4^{20} 0.8830; found M 223; calculated M 218.

Found %: C 82.32; H 10.36
$C_{15}H_{22}O$. Calculated %: C 82.50; H 10.01

Found %: OH 6.89 (Tserevitinov)
$C_{15}H_{22}O$. Calculated %: OH 7.8

The OH-group content was determined more accurately by the method of dehydration with iodine [6]; it amounted to 98% of theoretical.

Synthesis of 3,3-diphenyl-1-(cyclohexa-1',3'-dienyl)-prop-1-yn-3-ol

17.7 g of benzophenone, 10 g of 1-ethinylcyclohexa-1,3-diene, 10.5 g of C_2H_5Br, 2.3 g of Mg, and 100 ml of ether was allowed to react as above, giving 14 g of a fraction of b.p. 182-185°/26 mm; n_D^{20} 1.5810; d_4^{20} 1.0767; found M 290; calculated M 291.5.

Found %: C 87.86; H 6.04
$C_{21}H_{18}O$. Calculated %: C 88.10; H 6.30

Found %: OH 4.89 (Tserevitinov)
$C_{21}H_{18}O$. Calculated %: OH 5.85

---

* 2,3-Dihydrobenzoic acid melts at 94°, and its amide at 105°.

The OH content, determined by dehydration with iodine, was 96% of theoretical.

The presence of a triple bond in the alcohol was confirmed by its hydration; the 2,4-dinitrophenylhydrazone of the keto-alcohol so obtained melts at 182-183°.

Found %: N 11.76

$C_{27}H_{24}N_4O_5$. Calculated %: N 11.6

SUMMARY

1. 1-Ethinylcyclohexa-1,3-diene has been prepared, its physico-chemical properties have been studied, and its structure has been established from a study of its oxidation products.

2. Hydration of 1-ethinylcyclohexa-1,3-diene gives 1-acetylcyclohexa-1,3-diene, identified as its 2,4-dinitrophenylhydrazone, m.p. 230-230.5°.

3. The acetylenic alcohols 1-(cyclohex-1',3'-dienyl)-4-methyl-3-isopropylpent-1-yn-3-ol and 3,3-diphenyl-1-(cyclohexa-1',3'-dienyl)-prop-1-yn-3-ol have been prepared by the Iotsich-Grignard reaction, and their physico-chemical properties have been studied.

Received January 29, 1952

D. I. Mendeleev Chemico-Technological Institute

LITERATURE CITED

[1] S. V. Lebedev and S. R. Sergienko, J. Gen. Chem., 5, 1839 (1935).

[2] D. V. Tishchenko, J. Gen. Chem., 8, 1232 (1938).

[3] S. V. Lebedev, J. Russ. Chem. Soc., 45, 1249 (1913).

[4] N. M. Malenok, J. Gen. Chem., 9, 1952 (1939).

[5] A. Einhorn, Ber., 23, 2886 (1890) and 26, 454 (1893).

[6] O. V. Shvarts, Thesis, Moscow, 1949.

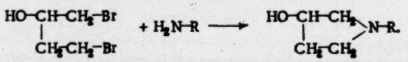
BLANK
PAGE

SYNTHESIS OF 1-ARYL-3-HYDROXYPYRROLIDINES

Yu. A. Arbuzov and L. I. Khmelnitsky

Although very many pyrrolidine compounds are known, there is little or no reference in the literature to 3-hydroxypyrrolidine and its N-substituted derivatives. We know only of a patent [1] which refers to the preparation of 3-hydroxy-1-arylpyrrolidines from 1,2,4-trihydroxybutane and primary arylamines; the patent gives no details of the preparation, and does not give the physical constants of the products.

The present paper describes a new method for synthesis of N-substituted 3-hydroxypyrrolidines by condensing primary amines with 1,4-dibromobutan-2-ol:



$$\begin{array}{l}HO\text{—}CH\text{—}CH_2\text{—}Br\\ \quad\;\;|\\ \quad CH_2\text{—}CH_2\text{—}Br\end{array} + H_2N\text{—}R \longrightarrow \begin{array}{l}HO\text{—}CH\text{—}CH_2\\ \quad\;\;|\qquad\quad\;\;\rangle N\text{—}R.\\ \quad CH_2\text{—}CH_2\end{array}$$

We applied this method to the synthesis of 3-hydroxy-1-phenyl- and 3-hydroxy-1-p-tolyl-pyrrolidine.

1,4-Dibromobutan-1-ol was prepared in the following way: allyl chloride, magnesium, and paraformaldehyde gave but-1-en-4-ol, by Yuriev's method [2], and this with phosphorus tribromide gave 4-bromobut-1-ene, which was treated with hypobromous acid, by the method of Likhosherstov [3]. Condensation of 1,4-dibromobutan-1-ol with aniline gave 3-hydroxy-1-phenylpyrrolidine (40% yield), a colorless substance, m.p. 96-97°. p-Toluidine similarly gave 3-hydroxy-1-p-tolylpyrrolidine (29% yield), a colorless crystalline substance, m.p. 84-85°.

EXPERIMENTAL

Preparation of 4-bromobut-1-ene

60 g of phosphorus tribromide (0.22 mol) was placed in a flask fitted with a stirrer with a mercury seal, a dropping funnel, a thermometer, and a reflux condenser with a calcium chloride tube, the flask was cooled in an ice-salt freezing mixture, and a mixture of 40 g (0.56 mol) of but-1-en-4-ol (b.p. 114-116°/779 mm) and 12 g (0.15 mol) of dry pyridine was added at such a rate that the reaction temperature did not exceed −5°. After all the reagents were mixed the solution was stirred for a further $2\frac{1}{2}$ hr at room temperature, the stirrer was disconnected, and the reflux condenser was replaced by an ordinary one. The contents of the flask were then distilled over, and the distillate was washed with 10% caustic potash, and then with water. It was then dried with fused calcium chloride, and redistilled, giving 56.2 g of 4-bromobut-1-ene, b.p. 96-99°/747 mm, yield 75% of theoretical.

Published data give b.p. 97-99° [4], 98.5-99°/758 mm [5], 97-102° [6].

Preparation of 1,4-dibromobutan-2-ol

A solution of 19.5 g of potassium hydroxide in 265 ml of water was added to 50 g of mercuric acetate, the precipitate was collected, washed free of alkali, and added in several portions to 41.4 g (0.26 mol) of bromine and 15.4 g (0.26 mol) of acetamide in 120 ml of water, shaking vigorously, and cooling under the tap, after each addition. The mixture was finally shaken for 20 min., and then filtered from mercuric bromide. The straw colored solution of N-bromacetamide was added to a thick-walled bottle containing 25 g (0.185 mol) of 4-bromobut-1-ene and 4 ml of glacial acetic acid, and the mixture was shaken for 12 hrs. The lower, oily layer was separated, and the aqueous layer was saturated with sodium chloride, and extracted with four portions of ether. The extracts were added to the oil, and the solution was dried with anhydrous sodium sulfate. The ether was then distilled off, and the residue was fractionally distilled in vacuum giving 25.8 g of 1,4-dibromobutan-2-ol, b.p. 107-110°/7 mm, d_4^{20} 1.9530; n_D^{20} 1.5444; found MR_D 37.51; calculated MR_D 37.73, yield 60%.

According to the literature [4], the b.p. is 114-115°/13 mm; d_0 2.023, d_{20} 1.96; n_D^{20} 1.544.

Preparation of 3-hydroxy-1-phenylpyrrolidine

Experiment 1. A mixture of 20 g (0.086 mol) of 1,4-dibromobutan-2-ol, 24.2 g (0.26 mol) of freshly distilled aniline, and 125 ml of dry benzene was heated for 16 hrs at 100°, under reflux, the flask was cooled, and 30 ml of 40% caustic potash was added. The benzene layer was separated, washed with water, benzene was distilled off at atmospheric pressure, and the aniline was distilled off under reduced pressure; the residue was distilled under 5 mm pressure, using an air condenser. The fraction boiling at 150-160° was collected, and was recrystallized from water, giving 5.3 g of 3-hydroxy-1-phenylpyrrolidine, m.p. 96-97°, bundles of colorless needles, yield 38%.

Found %: C 73.65; 73.53; H 8.03; 8.13; N 8.45; 8.41
$C_{10}H_{13}ON$. Calculated %: C 73.59; H 8.03; N 8.58

Acetylation with acetic anhydride gave 3-acetoxy-1-phenylpyrrolidine, a colorless viscous liquid, b.p. 129°/2 mm; d_4^{20} 1.1144; n_D^{20} 1.5603; found MR_D 59.58; calculated MR_D 57.41; EMR_D 2.17.

Found %: C 70.06; 70.00; H 7.32; 7.27; N 7.20; 7.21
$C_{12}H_{15}O_2N$. Calculated %: C 70.22; H 7.37; N 6.82

Experiment 2. A mixture of 20 g (0.086 mol) of 1,4-dibromobutan-2-ol and 24.2 g (0.26 mol) of freshly distilled aniline was heated under reflux at 100°. The flask was cooled after the reaction had begun, and after the initial violence of the reaction had moderated it was heated on a phosphoric acid bath, at 120°, for 4 hrs. The mixture was then cooled, and 30 ml of 40% caustic soda was added. The oily product separating was taken up in benzene, and the benzene was distilled off. The remaining operations were as in experiment 1, giving 5.6 g (40% yield) of 3-hydroxy-1-phenylpyrrolidine, m.p. 96-97°.

Preparation of 3-hydroxy-1-p-tolylpyrrolidine

A mixture of 36 g (0.336 mol) of freshly distilled toluidine, 25 g (0.108 mol) of 1,4-dibromobutan-2-ol, and 160 ml of dry benzene was heated under reflux on a water bath, for 15 hrs. The mixture was treated as before, benzene and aniline were distilled off, and the residue was distilled at 2 mm pressure, collecting the fraction boiling at 138-150°, which soon crystallized. Recrystallization from hot water gave 5.55 g (29% yield) of 3-hydroxy-1-p-tolylpyrrolidine, m.p. 84-85°, silky needles.

Found %: C 74.55; 74.65; H 8.66; 8.62; N 7.99; 8.12
$C_{11}H_{15}ON$. Calculated %: C 74.54; H 8.53; N 7.90

Received December 1, 1951

Institute of Organic Chemistry
Academy of Sciences USSR and
M.V. Lomonov, Moscow State University

LITERATURE CITED

[1] German Patent 742257; Chem. Abs. 40, 1179 (1948).

[2] Yu. K. Yuriev, G. B. Dubrovina, and E. I. Tregubov. J. Gen. Chem., 16, 843 (1946).

[3] M. V. Likhosherstov and S. V. Alekseev, . J. Gen. Chem. 3, 927 (1933).

[4] H. Pariselle, Am. Chim., [8] 24, 315 (1911).

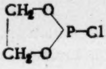
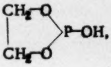
[5] A. Juvala, Ber., 63, 1989 (1930).

[6] R. P. Linstead, H. P. Rydon, J. Chem. Soc., 1995 (1934).

ESTERS OF "GLYCOLPHOSPHOROUS ACIDS"

COMMUNICATION 1. COMPOUNDS HAVING FIVE-, SEVEN, AND EIGHT-MEMBERED RINGS

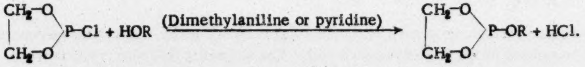
A. E. Arbuzov and V. M. Zoroastrova

The cyclic esters of phosphorous acid have received practically no study until recently. In the literature there are to be found only the reports by Carre [1] of his preparation in 1902 of the acid chloride of "ethylene-glycolphosphorous acid"  $\begin{array}{l}CH_2-O\\ |\\ CH_2-O\end{array}\!\!>\!P-Cl$ (ethylene phosphorochloridite) by the action of phosphorus trichloride on ethylene glycol and of the "ethylene-glycolphosphorous acid" itself (ethylene hydrogen phosphite)  $\begin{array}{l}CH_2-O\\ |\\ CH_2-O\end{array}\!\!>\!P-OH$, the barium salt of which was analyzed. Neither compound was isolated in a chemically pure form.

More detailed investigations into cyclic derivatives of phosphorous acid were commenced in our laboratory in 1945 [2]. In the present communication we give the results that we have obtained in a study of compounds containing five-, seven-, and eight-membered rings. By the action of phosphorus trichloride on ethylene glycol, 1,4-butanediol, and diethylene glycol in presence of substances that bind hydrogen chloride, we have synthesized the following phosphorochloridites (Table 1).

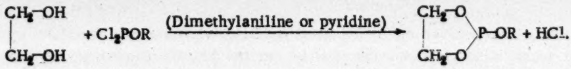
Ethylene phosphorochloridite (Compound 1) is a colorless liquid that fumes in air; it is similar in properties to diethyl phosphorochloridite. The phosphorochloridites derived from glycols in which the OH groups are separated by a chain of four or of five atoms (Compounds 2 and 3) contain seven- and eight-membered rings. They are very unstable: they fume strongly in air and, in a thin layer, ignite spontaneously and burn with a blue flame. In the pure state they are colorless liquids, but they rapidly polymerize, even in closed vessels, giving a colorless gelatinlike mass, which later becomes yellow with separation of red phosphorus.

By the action of alcohols in presence of pyridine or of dimethyl-aniline on cyclic phosphorochloridites, mixed cyclic esters are formed:



$$\begin{array}{l}CH_2-O\\ |\\ CH_2-O\end{array}\!\!>\!P-Cl + HOR \xrightarrow{\text{(Dimethylaniline or pyridine)}} \begin{array}{l}CH_2-O\\ |\\ CH_2-O\end{array}\!\!>\!P-OR + HCl.$$

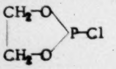
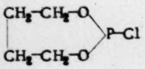
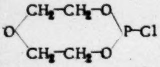
Cyclic esters of phosphorous acid may be obtained also by the action of glycols on Menshutkin's acid chloride in presence of the same acid-binding media:



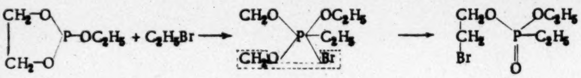
$$\begin{array}{l}CH_2-OH\\ |\\ CH_2-OH\end{array} + Cl_2POR \xrightarrow{\text{(Dimethylaniline or pyridine)}} \begin{array}{l}CH_2-O\\ |\\ CH_2-O\end{array}\!\!>\!P-OR + HCl.$$

Esters having a seven-membered ring were obtained by the latter method. We did not succeed in obtaining a mixed ester having an eight-membered ring. Six esters, obtained by one or other of the above methods, are listed in Table 2.

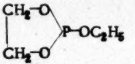
TABLE 1

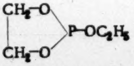
No.	Formula	B.p. °C	Pressure (mm Hg)	d_4^{20}	n_D^{20}	MR_D found	MR_D calculated
1		41.5	10	1.4172	1.4915	25.46	25.53
2		74-75.5	8	1.2858	1.5010	35.33	34.81
3		104-105	15	1.2693	1.5165	40.14	39.43

The physical and chemical properties of the esters obtained depend to a considerable extent on molecular size and structure: the compounds of low molecular weight are in many ways similar to trimethyl phosphite. The mixed cyclic esters of phosphorous acid are extremely reactive compounds. They react vigorously with cuprous halides, giving complex compounds. The CuI complexes of ethylene methyl phosphite and of ethyl ethylene phosphite were obtained in a crystalline form (Compound 1, m.p. 132-133°; Compound 2, m.p. about 90°). The cyclic esters react with sulfur with formation of thio esters. They react with water with evolution of much heat, and on coming into contact with concentrated nitric acid they burst into flame. One of the most interesting properties of cyclic phosphorous esters is their ability to react with many substances with opening of the ring. The reaction may be represented as follows:

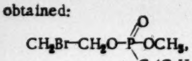
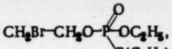
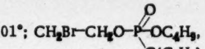


and is a special case of the Arbuzov rearrangement.

By the action of CH_3I on  there was obtained ethyl 2-iodoethyl methylphosphonate: b.p. 138-139°/10 mm; d_4^{20} 1.6783; n_D^{20} 1.4978; found MR_D 48.54; calculated MR_D 48.45. On hydrolysis with 10% hydrochloric acid it yielded methylphosphonic acid. The product of the reaction of CH_3I with ethylene methyl phosphite decomposed when distilled.

The action of C_2H_5Br on  yielded 2-bromoethyl ethyl ethylphosphonate, b.p. 129-139°/11 mm (dec.); d_4^{20} 1.3726; n_D^{20} 1.4610; found MR_D 48.98; calculated MR_D 48.17.

The reactions of the mixed ethylene-methyl, ethyl-ethylene, and butyl-ethylene esters of phosphorous acid with bromotriphenylmethane led also to rupture of the five-membered ring. The following reaction products were obtained:

 $CH_2Br{-}CH_2O{-}P(=O)(OCH_3){-}C(C_6H_5)_3$, b.p. 153-155°;  $CH_2Br{-}CH_2O{-}P(=O)(OC_2H_5){-}C(C_6H_5)_3$, b.p. 99-101°;  $CH_2Br{-}CH_2O{-}P(=O)(OC_4H_9){-}C(C_6H_5)_3$, b.p. 108-110°.

In the cases that we examined of reactions between the cyclic esters and halogen compounds, the yields were generally low, and they were never quantitative. It cannot therefore be asserted that the reaction proceeds exclusively in one direction, i.e., with rupture of the ring. The mixed ethylene-methyl and ethyl-ethylene esters of phosphorous acid were found to react energetically with acetyl chloride, but we did not succeed in isolating individual compounds owing to decomposition of the reaction products when vacuum-distilled. The analytical figures for chlorine in the fractions separated differed from the calculated values by 2-3%.

By treatment with water, ethyl ethylene phosphite yielded a product corresponding in analysis to

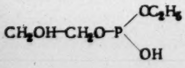
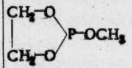
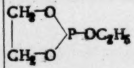
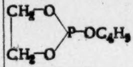
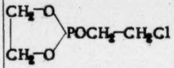
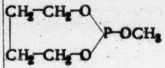
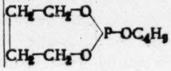
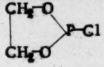
 $CH_2OH{-}CH_2O{-}P(OC_2H_5)(OH)$, b.p. 142-143°/11 mm; n_D^{20} 1.4825. It was a very viscous, colorless liquid.

TABLE 2

No.	Formula	B.p. °C	Pressure (mm Hg)	d_4^{20}	n_D^{20}	MR_D	
						found	calculated
1		55-56	23	1.2159	1.4460	26.77	26.91
2		51-51.5	15	1.1317	1.4395	31.66	31.62
3		71-72	8.5	1.0819	1.4470	40.53	40.82
4		78.5-79.5	6.5	1.3206	1.4755	36.39	36.41
5		54-55	4.5-5	1.1640	1.4642	35.60	36.15
6		100-102	9-10	1.0557	1.4540	49.28	50.00

EXPERIMENTAL

1. Preparation of



Ethylene glycol (77.5 g), dimethylaniline (302.7 g), and dry ether (700 ml) were placed in a two-liter round-bottomed flask fitted with reflux condenser and dropping funnel. The mixture was stirred mechanically and cooled by surrounding the flask with iced water. Freshly distilled phosphorus trichloride (171.7 g) was added dropwise to the mixture. At first, the dimethylaniline hydrochloride formed in the reaction came out in the form of an oil, and this crystallized out only after one-third of the required amount of phosphorus trichloride had been added. Subsequently, the dimethylaniline hydrochloride formed crystallized out immediately. When the whole of the phosphorus trichloride had been added, stirring was continued for a further 45 minutes. The precipitate was then filtered off under suction and was washed well with dry ether. Solvent was distilled off from the filtrate, which was then vacuum-fractionated. The product (113.7 g) had b.p. 38-56°/9 mm; a residue of 21 g remained in the flask. Redistillation through a Widmer column yielded a fraction (101.2 g, 64%) of b.p. 41.5°/10 mm, d_4^{20} 1.4172; n_D^{20} 1.4950; found MR_D 25.46; calculated MR_D 25.58. The substance was a colorless mobile liquid, soluble in organic solvents. It fumed in air and reacted vigorously with water. It was oxidized by concentrated nitric acid with deflagration.

Found %: Cl 27.99

$C_2H_4O_2PCl$. Calculated %: Cl 28.02

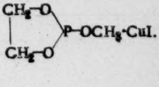
2. Preparation of Ethylene Methyl Phosphite

The materials taken for reaction were ethylene phosphorochloridite (46 g), absolute methanol (11.64 g, i.e. one mole per mole of the chlorido compound), and dimethyl aniline (44.03 g); the methanol and dimethylaniline were dissolved in dry ether (300-280 ml). Ethylene phosphorochloridite, diluted with an equal amount of dry ether, was added dropwise to the snow-cooled solution, which was constantly stirred. As reaction proceeded, the mixture grew warm and a colorless oil separated (dimethylaniline hydrochloride); the latter soon began to crystallize. When the whole of the chlorido compound had been added, the mixture was stirred for a further 20 minutes. The precipitate was filtered off and washed three times with dry ether. The ether solution was fractionated from an Arbuzov flask having two bulbs. After two fractionations a product (21.75 g, 49%) was obtained having b.p. 55-56°/23 mm; d_4^{20} 1.2159; n_D^{20} 1.4460; found MR_D 26.77; calculated MR_D 26.91.

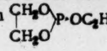
The product was a colorless, very mobile liquid having a very pleasant odor similar to that of trimethyl phosphite; it was soluble in many organic solvents. It reacted with water, producing much heat, and it burst into flame on coming into contact with concentrated nitric acid.

Found %: P 25.33; 25.28

$C_3H_7O_3P$. Calculated %: P 25.41

It reacted with CuI with formation of a crystalline substance, m.p. 132-133° (from chloroform) 

3. Preparation of Ethyl Ethylene Phosphite

Ethylene phosphorochloridite was added dropwise to a mixture of absolute alcohol (19.27 g), dimethylaniline (50.73 g), and dry ether (300 ml) (mechanical stirring, cooling with snow). Almost from the first drop of the phosphorochloridite a precipitate of dimethylaniline hydrochloride began to form. When the whole of the phosphorochloridite had been added and stirring had been continued for 35 minutes, the reaction was regarded as finished. The dimethylaniline hydrochloride was filtered off, and the filtrate was vacuum-distilled from an Arbuzov flask having two bulbs. The product (31.93 g, 56%) had b.p. 51-51.5°/15 mm; d_4^{20} 1.1317; n_D^{20} 1.4395; found MR_D 31.66; calculated MR_D 31.62. The compound was similar in appearance to ethylene methyl phosphite and had a characteristic odor, not so pleasant as that of the methyl compound. It was oxidized by concentrated nitric acid with deflagration. It formed a complex compound of composition  $\begin{matrix}CH_2O\\ |\\ CH_2O\end{matrix}\!\!>P\cdot OC_2H_5\cdot CuI$, m.p. about 90°, unstable in air.

Found %: P 22.89
$C_4H_9O_3P$. Calculated %: P 22.79

4. Preparation of Butyl Ethylene Phosphite

Butyl ethylene phosphite was prepared via Menshutkin's acid chloride. Pyridine was used in place of dimethylaniline, for the boiling point of dimethylaniline is close to that of butyl ethylene phosphite. The materials taken for reaction were: $C_4H_9OPCl_2$ (58.2 g), ethylene glycol (20.62 g), and pyridine (52.57 g). The $C_4H_9OPCl_2$, diluted with an equal volume of dry ether, was added dropwise to a solution in dry ether (300 ml) of the ethylene glycol and pyridine (mechanical stirring, cooling with snow). Pyridine hydrochloride did not begin to crystallize out immediately; crystallization began only after about one-fifth of the necessary amount of acid chloride had been added. The latter was added over one hour, and the mixture was then stirred further at room temperature for 30 minutes. Fractionation of the reaction products (after separation of the precipitate and removal of solvent) yielded a substance (24 g, 44.3% of b.p. 71-72°/8.5 mm, d_4^{20} 1.0819; n_D^{20} 1.4470; found MR_D 40.53; calculated MR_D 40.87. The product was an oily liquid of characteristic odor; it was more viscous than the previous esters.

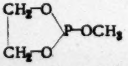
Found %: P 18.68; 18.86
$C_6H_{13}O_3P$. Calculated %: P 18.90

5. Preparation of 2-Chloroethyl Ethylene Phosphite

A mixture of 2-chloroethanol (31.81 g), pyridine (31.24 g), and dry ether (300 ml) was placed in a one-liter flask fitted with reflux condenser, mechanical stirrer, and dropping funnel; the flask was cooled externally with snow. Ethylene phosphorochloridite (50 g), diluted with an equal volume of dry ether, was added over one hour under constant stirring. With the addition of the first drops of phosphorochloridite, a crystalline precipitate of pyridine hydrochloride began to separate from the reaction mixture. The temperature in the flask did not exceed 5°. When the whole of the phosphorochloridite had been added, the reaction mixture was stirred for 15 minutes. The mixture was then allowed to stand without stirring for two hours at room temperature. The pyridine salt was filtered off, and the filtrate was vacuum-fractionated through a Widmer column. A fraction of b.p. 78.5-79.5°/6.5 mm (50 g, 74%) was obtained; d_4^{20} 1.3206; n_D^{20} 1.4755; found MR_D 36.39; calculated MR_D 36.41. It was an oily liquid of characteristic odor, soluble, like the previous esters, in many organic solvents. It reacted vigorously with water.

Found %: Cl 20.62
$C_4H_8O_3PCl$. Calculated %: Cl 20.79

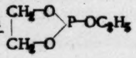
Action of Alkyl Halides on the Esters

1. Action of Methyl Iodide on  $\begin{matrix}CH_2-O\\ |\\ CH_2-O\end{matrix}\!\!>P-OCH_3$

A mixture of ethylene methyl phosphite (6.7 g) and methyl iodide (7.8 g, i.e. one mole per mole of ester) was sealed in a tube (the tube was drawn out at one end; the meniscus was in the narrow part of the tube and its position was marked by pencil before the experiment). The tube was allowed to stand at room temperature for 24 hours, when a small diminution in the volume of mixture could be observed. When the tube had been heated at

40° for seven hours and at 60° for one hour, reaction was considered to be complete. When the tube was opened, the odor of the original ester could not be detected. The reaction product was distilled. About 2 g of methyl iodide and 3.7 g of a fraction of b.p. 100-130°/4-5 mm (dec.) (a viscous liquid having an intense iodine color) were obtained. Considerable decomposition was again observed when this fraction was redistilled. We did not succeed in separating any individual substances.

2. Action of Methyl Iodide on



$$\begin{array}{l} CH_2{-}O \\ | \\ CH_2{-}O \end{array}\!\!>P{-}OC_2H_5$$

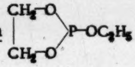
A mixture of ethyl ethylene phosphite (4.23 g) and methyl iodide (4.41 g) was heated in a sealed tube at 50-60° for 6.5 hrs. The contents of the tube took up the color of iodine. When they were distilled, a red product (2.65 g, 30.6%), b.p. 138-139°/10 mm, was obtained; it was soluble in ether, benzene, and alcohol and had d_4^{20} 1.6783; n_D^{20} 1.4978; found MR_D 48.54; calculated MR_D 48.45.

Found %: I 45.48; 45.55

$C_5H_{12}O_3PI$. Calculated %: I 45.65

Hydrolysis of product of b.p. 138-139°/10 mm. The product (0.9 g) was heated with 10% hydrochloric acid (10 ml) in a sealed tube at 140° for six hours. Crystals of m.p. 103-105° were obtained (m.p. of methylphosphonic acid: 105°).

3. Action of Ethyl Bromide on



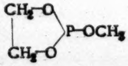
$$\begin{array}{l} CH_2{-}O \\ | \\ CH_2{-}O \end{array}\!\!>P{-}OC_2H_5$$

A mixture of ethyl ethylene phosphite (6.8 g) and ethyl bromide (5.4 g, i.e. one mole per mole of ester) was heated in a sealed tube at 100° for 16 hours. The reaction did not go to completion; the odor of the original ester persisted. Heating of the mixture was continued at 130° for 15 hours. As a result of two fractionations of the reaction products, a fraction (3.8 g, about 35%) was separated having b.p. 129-130°/11 mm (dec); d_0^{20} 1.3726; n_D^{20} 1.4610; found MR_D 48.98; calculated MR_D 48.17. It was a colorless, almost odorless liquid, soluble in the usual organic solvents.

Found %: Br 32.44

$C_6H_{14}O_3PBr$. Calculated %: Br 32.61

4. Action of $(C_6H_5)_3CBr$ on



$$\begin{array}{l} CH_2{-}O \\ | \\ CH_2{-}O \end{array}\!\!>P{-}OCH_3$$

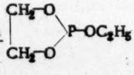
A mixture of $(C_6H_5)_3CBr$ (1 g) and ethylene methyl phosphite (0.37 g, i.e. 1 mol. equiv.) was dissolved in dry benzene (4 ml), and the solution was boiled under reflux for 20 minutes. When reaction was complete, part of the benzene was driven off. The reaction mass crystallized on standing, and the crystals were filtered off and washed with ligroin. After three recrystallizations from a benzene-gasoline mixture, fine colorless prisms, m.p. 153-155°, were obtained. The product was of good solubility in ether, benzene, and chloroform.

Found %: Br 17.15

$C_{22}H_{22}O_3PBr$. Calculated %: Br 17.55

Hydrolysis of the reaction product. Some of the product of m.p. 153-155° (0.1 g) was heated in a sealed tube with 10% hydrochloric acid (2 ml) at 180° for five hours. Crystals of triphenylmethylphosphonic acid, m.p. 276-280°, were obtained.

5. Action of $(C_6H_5)_3CBr$ on

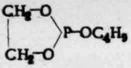


$$\begin{array}{l} CH_2{-}O \\ | \\ CH_2{-}O \end{array}\!\!>P{-}OC_2H_5$$

A solution of bromotriphenylmethane (1 g) and ethyl ethylene phosphite (0.38 g) in dry benzene was boiled for 25 minutes. After removal of a part of the benzene, the mixture was poured into a dish and set aside for crystallization, which occurred in the course of a day. The substance was recrystallized from a mixture of benzene and gasoline (0.9 g, m.p. 99-101°). It was similar in its properties to the previous product.

Hydrolysis of the reaction product. Some of the product (0.2 g) was heated with hydrochloric acid (7 ml) at 170-180° for five hours. Triphenylmethylphosphonic acid, m.p. 275-279°, was obtained.

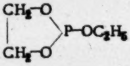
6. Action of $(C_6H_5)_3CBr$ on



A solution of butyl ethylene phosphite (1.8 g) and bromotriphenylmethane (3.5 g) in dry benzene was heated for 30 minutes. When reaction was complete, the mixture was allowed to stand in a desiccator, when a crystalline precipitate (2.9 g) quickly formed. The product was purified by recrystallization from benzene-gasoline. It formed fine colorless crystals, m.p. 108-110°, readily soluble in ether, benzene, ethyl acetate, and other solvents.

Found %: Br 16.20
$C_{25}H_{28}O_3PBr$. Calculated %: Br 16.40

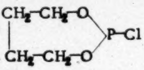
7. Action of Water on



Ethyl ethylene phosphite (9.06 g) was placed in a small Arbuzov flask, and water (1.2 g), slightly acidified with hydrochloric acid, was added carefully. There was a vigorous reaction: the temperature of the mixture rose to 83° with formation of an apparently homogeneous solution. This was vacuum-distilled twice, yielding a colorless viscous liquid (3.5 g; b.p. 142-144°/11 mm, n_D^{20} 1.4825), which according to the results of analysis for phosphorus, was the product of the reaction of one molecule of ethyl ethylene phosphite with one molecule of water. The product was soluble in methanol, ethanol, acetone, and water, but not very soluble in ether and benzene.

Found %: P 20.53; 20.28
$C_4H_{11}O_4P$. Calculated %: P 20.12

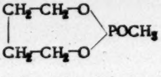
8. Preparation of



Freshly distilled phosphorus trichloride (137.42 g) was added dropwise under mechanical stirring to a mixture of 1,4-butanediol (90.08 g: 1.4 mol. equiv.), dimethylaniline (242.2 g), and dry ether (one liter). The mixture was cooled externally with snow. A precipitate of dimethylaniline hydrochloride began to appear soon after the addition of a small amount of phosphorus trichloride. When reaction was complete, the mixture was allowed to stand at room temperature for one hour. The precipitate was then filtered off and the filtrate was vacuum-distilled. As a result of four distillations (the last through a Widmer column) a product (6.1 g, 10% *) was obtained having b.p. 74-75.5°/8 mm (dec). d_0^{20} 1.2885; n_D^{20} 1.5010; found MR_D 35.55; calculated MR_D 34.81. It was a colorless liquid, which burst into flames in the air and burned with a blue flame. After being kept for three days in a sealed tube it polymerized to a colorless transparent mass, from which a yellow precipitate of phosphorus subsequently separated.

Found %: Cl 23.33
$C_4H_8O_2PCl$. Calculated %: Cl 22.88

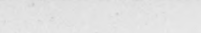
9. Preparation of



Methyl phosphorodichloridite (b.p. 90-92°) (61.1 g) was added to a solution of 1,4-butanediol (41.38 g) and pyridine (72.63 g) in dry ether (200 ml) (mechanical stirring, cooling with snow). The products were worked up in the usual way, and a liquid, boiling at 54-55°/4.5-5 mm, and having d_0^{20} 1.1640 and n_D^{20} 1.4642, was obtained (2 g, about 3%). MR_D: found 35.60; calculated 36.20. The greater part of the products polymerized in the distillation flask as a colorless, jellylike mass.

Found %: P 20.40
$C_5H_{11}O_3P$. Calculated %: P 20.66

The ester obtained was a colorless liquid of characteristic odor. It formed an unstable crystalline addition product with cuprous iodide:



m.p. 142-144° (from benzene-gasoline).

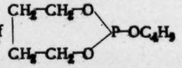
---

* After every distillation, there remained a large amount of red phosphorus in the distillation flask.

Found %: I 36.93

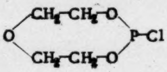
$C_5H_{11}O_3PCuI$. Calculated %: I 37.15

10. Preparation of



Butyl tetramethylene phosphite was prepared by a method similar to that used for the preceding ester from Menshutkin's acid chloride and the glycol in presence of pyridine. The materials taken for reaction were: $C_4H_9OPCl_2$ (24 g), 1,4-butanediol (12.35 g), and pyridine (21.66 g). Fractionation of the reaction products yielded a substance of b.p. 100-102°/9-10 mm; d_0^{20} 1.0557; n_D^{20} 1.4540; found MR_D 49.28; calculated MR_D 50.00; (2.96 g, 11%). It was a colorless liquid with a faint odor, very unstable to storage.

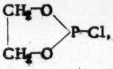
11. Preparation of

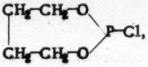


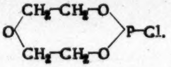
This compound was prepared by a method similar to that used for the other chlorido compounds from diethylene glycol (38 g) and phosphorus trichloride (49.07 g) in presence of dimethylaniline and in a medium of dry ether (500 ml) After a number of fractionations, 3 g (5%) of a product of b.p. 104-105°/15 mm; d_0^{20} 1.2693; n_D^{20} 1.5165; found MR_D 40.14; calculated MR_D 39.43; was isolated. It was a thick oily colorless substance and was very unstable, burning spontaneously in the air with a bluish flame (compare the phosphorochloridites having a seven-membered ring).

SUMMARY

1. A study has been made of the action of ethylene glycol, of 1,4-butanediol, and of diethylene glycol on phosphorus trichloride in presence of substances that bind hydrogen chloride. Cyclic esters of phosphorochloridous acid having five-, seven-, and eight-membered rings have been synthesized:







2. By the action of alcohols on the phosphorochloridites, and also by the action of glycols on Menshutkin's acid chloride, mixed cyclic esters of phosphorous acid have been prepared; some of their properties have been studied.

Received June 23, 1952

A. M. Butlerov Chemical Research Institute
of the V. I. Ulyanov-Lenin Kazan State Univ.

LITERATURE CITED

[1] P. Carre, Bull (3), 27, 264 (1902).

[2] A. E. Arbuzov, Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 2, 226 (1946).

BLANK
PAGE

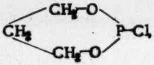
ESTERS OF "GLYCOLPHOSPHOROUS ACIDS"

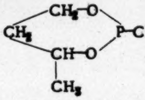
COMMUNICATION 2. COMPOUNDS HAVING A SIX-MEMBERED RING

A. E. Arbuzov and V. M. Zoroastrova

In Communication 1 [1] we have described five-, seven-, and eight-membered cyclic derivatives of phosphorous acid prepared by us from α- and γ-glycols and from diethylene glycol. In the course of investigations in this field we have studied also compounds having a six-membered ring. In the present communication we give the results of our investigations of compounds prepared from β-glycols and containing, therefore, a six-membered ring.

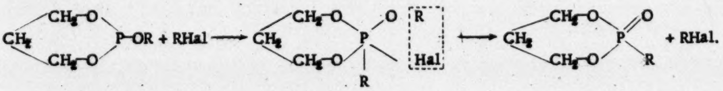
By the action of 1,3-propanediol and of 1,3-butanediol on phosphorus trichloride in presence of dimethylaniline we have obtained:

1. Trimethylene phosphorochloridite  b.p. 70-71° at 17 mm; d_4^{20} 1.3407; n_D^{20} 1.4850; found MR_D 30.03; calculated MR_D 30.21, yield 67.5%.

2. 1-Methyltrimethylene phosphorochloridite  b.p. 65° at 12 mm; d_4^{20} 1.2496; n_D^{20} 1.4765; found MR_D 34.91; calculated MR_D 34.81. Compound 2 was obtained in high yield (81%). It is unique in its high stability in comparison with all the other cyclic phosphorochloridites that we have studied.

By reaction with hydroxy compounds, the phosphorochloridite exchanges its halogen for a hydroxyl or methoxyl group. Reaction with alcohols in presence of substances that bind hydrogen chloride, in a medium of dry ether or other indifferent solvent, leads to ester formation. The physical properties of the resulting mixed cyclic esters of phosphorous acid are given in Table 1.

When they react with alkyl halides, these six-membered cyclic esters undergo isomerization: the ring remains intact, and cyclic esters of alkylphosphonic acids are formed. The reaction is represented by A. E. Arbuzov's scheme:



The isomerization products are given in Table 2.

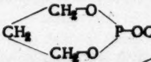
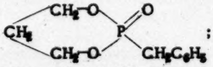
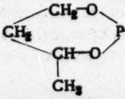
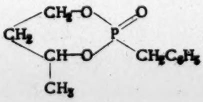
When reaction occurs with benzyl chloride or bromide, the ring of the ester again remains intact. Reaction of  with $C_6H_5CH_2Cl$ yields the compound ; b.p. 138-139°. By the action on  (where R = CH_3, C_2H_5, C_4H_9) of benzyl chloride or bromide, a product of m.p. 120-121° is formed; the analytical results correspond to .

TABLE 1

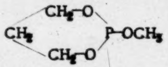
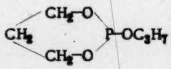
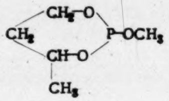
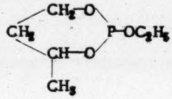
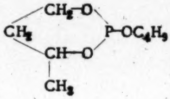
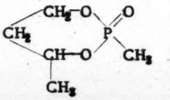
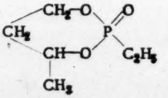
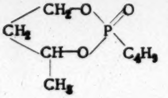
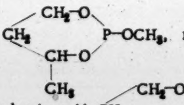
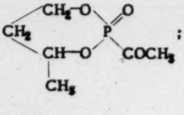
No.	Formula	B.p. °C	Pressure (mm Hg)	d_0^{20}	n_D^{20}	MR_D	
						found	calculated
1		65-66 (50-51)	23 11	1.1758	1.4465	31.46	31.59
2		69	9	1.0582	1.4452	41.29	40.77
3		62	13	1.1092	1.4420	35.80	36.15
4		63-64	8	1.0696	1.4410	40.51	40.77
5		75-76	3.5-4	1.0252	1.4472	50.00	50.01

TABLE 2

No.	Formula	B.p. °C	Pressure (mm Hg)	d_0^{20}	n_D^{20}	MR_D	
						found	calculated
1		117-119	7	1.2031	1.4500	33.52	33.44
2		123	5	1.1541	1.4510	38.29	38.06
3		127	5	1.1039	1.4538	47.11	47.25

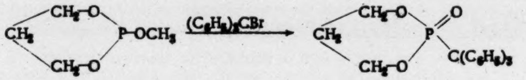
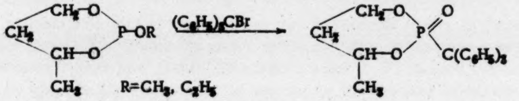
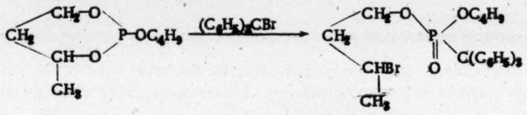
An interesting result was obtained in the study of the reaction of the esters with bromotriphenylmethane. By reaction with $(C_6H_5)_3CBr$, methyl (or ethyl) trimethylene (or 1-methyltrimethylene) phosphite yielded esters of triphenylmethylphosphonic acid. Butyl 1-methyltrimethylene phosphite reacted with the same compound with opening of the ring (Table 3).

The methyl ester , reacted with acetyl bromide, giving a satisfactory yield of a cyclic ester of acetylphosphonic acid  ; b.p. 142-143° at 4-3.5 mm; d_0^{20} 1.2574; n_D^{20}

1.4555; found MR_D 38.20; calculated MR_D 38.10.

The action of water on the esters was tried, and it was found that reaction proceeds with preservation of the ring, leading to formation of cyclic acids. The ring remains intact also when the phosphorochloridites react with water.

TABLE 3

No.	Formula	B.p. °C
1		228-229
2		192-193
3		109-110

EXPERIMENTAL

1. Preparation of Trimethylene Phosphorochloridite

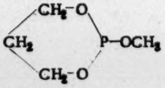
The materials taken for recreation were 1,3-propanediol (100 g), phosphorus trichloride (180.6 g), and dimethylaniline (318.4 g). Since 1,3-propanediol is of low solubility in ether, the reaction was carried out in a mixture of dry dioxane and dry ether. The 1,3-propanediol and dimethylaniline were dissolved in a 1:1 mixture of dioxane and ether (700 ml), and before commencing the reaction a few crystals of dimethylaniline hydrochloride were added to the solution. Freshly distilled phosphorus trichloride (180.6 g) was added dropwise to the solution, which was cooled with snow. The filtrate, after removal of the precipitated dimethylaniline hydrochloride, was fractionated through a Widmer column, yielding a product (124 g, 67.5 %) boiling at 70-71°/17 mm, and having d_4^{20} 1.3407; n_D^{20} 1,4850; found MR_D 30.03; calculated MR_D 30.21. It is a colorless oily liquid that fumes in air.

Found %: P 22.21
$C_3H_6O_2PCl$. Calculated %: P 22.06

2. Preparation of 1-Methyltrimethylene Phosphorochloridite

A mixture of 1,3-butanediol (90 g), dimethylaniline (242.5 g), and dry ether (one liter) was introduced into a two-liter round-bottomed flask fitted with reflux condenser and mechanical stirrer. The reaction mixture was cooled with water containing snow. Freshly distilled phosphorus trichloride (137.42 g), diluted with an equal volume of dry ether, was added dropwise under constant stirring. When reaction was complete, the dimethylaniline hydrochloride was filtered off and washed three or four times with dry ether. The product, after removal of the ether, was vacuum-distilled from an Arbuzov flask. After a second distillation, a product (125 g, 81%) was obtained boiling at 65°/12mm, having the following constants: d_4^{20} 1.2496; n_D^{20} 1.4765; found MR_D 34.91; calculated MR_D 34.81. It is a colorless oily liquid, soluble in organic solvents. It fumes in air, but can be preserved unchanged in a sealed tube.

Found %: Cl 22.71
$C_4H_8O_2PCl$. Calculated %: Cl 22.81

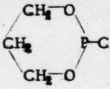
3. Preparation of 

Trimethylene phosphorochloridite (63.2 g) was added to a mechanically stirred solution of absolute methanol (12.4 g) and anhydrous pyridine (35.55 g) in dry ether (150 ml) contained in a flask that was cooled externally with snow. With the first few drops of the phosphorochloridite a crystalline precipitate of pyridine hydrochloride began to appear. When reaction was complete, the pyridine hydrochloride was filtered off and the filtrate was vacuum-distilled. After a second distillation, a liquid (45.6 g, 61.2%) was obtained having B.p. 65-66° at 23 mm (50-51° at 11 mm) 45.6 g, or 61.2% of theory: d_4^{20} 1.1758; n_D^{20} 1.4465; found MR_D 31.46; calculated MR_D 31.59.

Found %: P 22.78

$C_4H_9O_3P$. Calculated %: P 22.79

4. Preparation of Propyl Trimethylene Phosphite

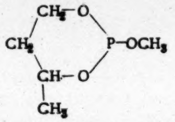
The compound was prepared by a method similar to that used for the previous compound from the phosphorochloridite  (22.8 g), propyl alcohol (9.72 g), and pyridine (12.82 g) in a medium of dry ether (200 ml). The product (12 g 45%) b.p. 69° at 9 mm; d_4^{20} 1.0582; n_D^{20} 1.4452; found MR_D 41.29; calculated MR_D 40.77. It was a colorless oily liquid, soluble in organic solvents. It reacted with cuprous halides with evolution of heat (we did not succeed in isolating crystalline products).

Found %: P 18.51

$C_6H_{13}O_3P$. Calculated %: P 18.90

In addition to the product of b.p. 69°/9 mm, 2 g of a fraction boiling at 168-169°/12 mm (n_D^{20} 1.4625; d_4^{20} 1.2231), was isolated. Attempts to determine its structure were not successful (analysis for phosphorus gave 23.33% P).

5. Preparation of the Ester



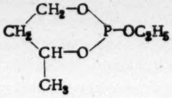
A mixture of absolute methanol (12.7 g), pyridine (31.85 g), and dry ether (300 ml) was cooled to 5°. The phosphorochloridite (61.3 g), diluted with an equal amount of dry ether, was added to the solution (mechanical stirring and cooling with snow). The reaction continued for 1 hour 30 minutes, and the mixture was then allowed to stand at room temperature for 30 minutes, after which pyridine hydrochloride was filtered off. Vacuum fractionation of the filtrate from an Arbuzov flask yielded a product (37.7 g, 60%) having b.p. 62°/13 mm, d_4^{20} 1.1092; n_D^{20} 1.4420; found MR_D 35.80; calculated MR_D 36.15. It was a colorless liquid having an unpleasant odor similar to that of trimethyl phosphite.

Found %: P 20.40

$C_5H_{11}O_3P$. Calculated %: P 20.66

The same ester (b.p. 64° at 16 mm; n_D^{20} 1.4422) was obtained by reaction in ether solution of CH_3OPCl_2 with 1,3-butanediol in presence of pyridine, but the yield was lower (37.3%).

6. Preparation of the Ester

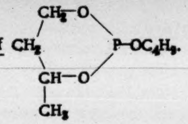


The phosphorochloridite (50 g), diluted with an equal volume of dry ether, was added dropwise to a cooled (to 5°) mixture of absolute ethanol (14.88 g), pyridine (25.64 g), and dry ether (250 ml). When reaction was complete, the flask was allowed to stand for 30 minutes at room temperature; the pyridine salt was then filtered off, and the filtrate was vacuum-distilled from an Arbuzov flask. After a second distillation a product (40.65 g, 76.5%) was obtained having b.p. 63-64° at 8 mm; d_4^{20} 1.0696; n_D^{20} 1.4410; found MR_D 40.51; calculated MR_D 40.77. It was a colorless, transparent liquid of characteristic odor, soluble in ether, benzene, and chloroform. It reacted with cuprous halides (with CuI it yielded a crystalline product, m.p. 135° (from absolute alcohol). It reacted vigorously with water that had been slightly acidified with hydrochloric acid.

Found %: P 18.70; 18.60

$C_6H_{13}O_3P$. Calculated %: P 18.90.

7. Preparation of



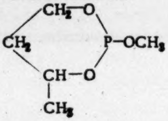
Butyl 1-methyltrimethylene phosphite was prepared from Menshutkin's acid chloride and 1,3-butanediol in presence of dimethylaniline. A solution of 1,3-butanediol (52.65 g) and dimethylaniline (144.8 g) in a mixture of dry benzene (700 ml) and anhydrous dioxane (150 ml) was cooled with snow (before the beginning of the reaction, about 1 g of dimethylaniline hydrochloride was introduced). Butyl phosphorodichloridite (101.7 g) was added dropwise to this solution. The reaction products were worked up in the usual way, and the butyl ester obtained (60.4 g, 54.1%) had b.p. 75-76° at 3.5-4mm; d_4^{20} 1.0252; n_D^{20} 1.4472; found MR_D 50.00; calculated MR_D 50.01. It was a colorless oily liquid, more viscous than the preceding esters, and having an odor characteristic of butyl esters.

Found %: P 15.99; 16.16

$C_8H_{17}O_3P$. Calculated %: P 16.13

8. Action of Alkyl Halides on the Esters

1. Action of methyl iodide on

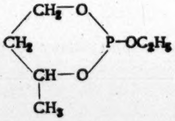


The methyl ester (10.9 g) and methyl iodide (10.31 g) were sealed in a tube (slight warming up was observed). The mixture was heated at 100° for two hours. After methyl iodide (about 6 g) had been driven off, the products were vacuum-distilled twice. A substance (6 g, 58%) was obtained having b.p.117-119° at 7 mm; d_4^{20} 1.2031; n_D^{20} 1.4500; found MR_D 33.52; calculated MR_D 33.44. It was a colorless oily substance, more viscous than the original methyl ester, and practically without odor. It was soluble in alcohol, ether, benzene and water.

Found %: C 39.49; 39.58; H 7.28; 7.48

$C_5H_{11}O_3P$. Calculated %: C 39.97; H 7.38

2. Action of ethyl iodide on

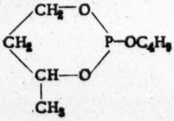


The ethyl ester (12 g) and ethyl iodide (11.45 g) were sealed in a tube (no reaction was to be observed at ordinary temperature). The tube was heated in a boiling water bath for five hours. Fractionation of the reaction products gave ethyl iodide (10 g) and a product (5 g, 41.7%) having b.p. 123° at 5 mm; d_4^{20} 1.1541; n_D^{20} 1.4520; found MR_D 38.29: Calculated MR_D 38.01.

Found %: C 43.39; H 7.99

$C_6H_{13}O_3P$. Calculated %: C 43.87; H 7.98

3. Action of butyl bromide on



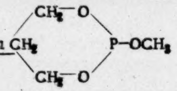
Butyl 1-methyltrimethylene phosphite (14 g) and butyl bromide (10.4 g) were heated in a sealed tube at 150-160° for 5 hours 30 minutes. After a number of vacuum distillations, a product (4.5 g, 32.1%) was obtained having b.p. 127° at 5 mm; d_4^{20} 1.1039; n_D^{20} 1.4538; found MR_D 47.11; calculated MR_D 47.25.

Found %: P 15.82; 15.85

$C_8H_{17}O_3P$. Calculated %: P 16.13

9. Action of Bromotriphenylmethane on the Esters

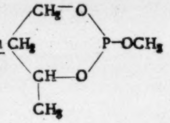
1. Action of $(C_6H_5)_3CBr$ on



A solution of methyl trimethylene phosphite (0.68 g) and bromotriphenylmethane (1.5 g) in benzene (3 ml) was boiled for 20 minutes. The reaction mixture crystallized out when half of the benzene had been driven off. The product was purified by recrystallization from dioxane; it had m.p. 227-228°.

Found %: C 72.12; H 5.80; P 8.70
$C_{22}H_{21}O_3P$. Calculated %: C 72.49; H 5.81; P 8.51

2. Action of $(C_6H_5)_3CBr$ on

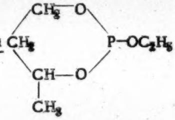


The methyl ester (0.75 g), bromotriphenylmethane (0.61 g), and dry benzene (4 ml) were placed in a 5-ml Arbuzov flask, and the mixture was boiled cautiously for 30 minutes. Part of the benzene was driven off, and 3-4 ml of gasoline was added. The mixture was cooled with snow, and a fine crystalline precipitate was formed. The product melted, after recrystallization from a benzene-gasoline mixture, at 192-193°. It was similar to the preceding product in properties.

Found %: C 72.30; H 6.06; P 8.61
$C_{23}H_{23}O_3P$. Calculated %: C 72.97; H 6.12; P 8.20

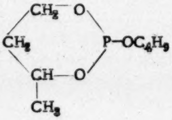
Hydrolysis of product of m.p. 192-193°: The product (0.2 g) and 20% hydrochloric acid (5 ml) were heated in a sealed tube at 180° for five hours. Crystals of triphenylmethylphosphonic acid (m.p. 276-279°) were obtained.

3. Action of $(C_6H_5)_3CBr$ on



A mixture of the ethyl ester (0.82 g), bromotriphenylmethane (1.5 g), and dry benzene (5 ml) was heated in an Arbuzov flask for 45 minutes. The reaction products were worked up as before and yielded a small amount of crystals of m.p. 192-193°. In admixture with the preceding product it melted without depression.

4. Action of $(C_6H_5)CBr$ on

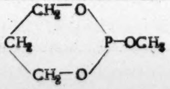


For the reaction 1.99 g of the butyl ester and 3.23 g of bromotriphenylmethane were taken. The benzene solution was heated for 20 minutes, and gasoline (5 ml) was then added. A halogen-containing product of m.p. ~110° was obtained.

Found %: P 6.28; Br 15.58
$C_{27}H_{32}O_3PBr$. Calculated %: P 6.01; Br 15.51

10. Action of Benzyl Chloride and Bromide on the Esters

1. Action of $C_6H_5CH_2Cl$ on

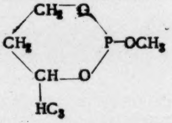


Methyl trimethylene phosphite (6.6 g) and benzyl chloride (6.1 g) were heated in a sealed tube at 100°

for 3 hours 30 minutes. The reaction did not go to completion (the odor of the original ester persisted). Heating was continued at 140-150° for four hours. When the tube was opened, vigorous frothing, due to the evolution of methyl chloride, occurred. The reaction product rapidly crystallized out, yielding a compact mass. After recrystallization from benzene, the substance melted at 138-139°.

Found %: C 56.20; H 5.93; P 14.65
$C_{10}H_{13}O_3P$. Calculated %: C 56.57; H 6.17; P 14.62

2. Action of benzyl chloride on

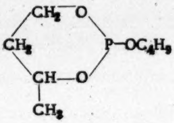


A mixture of the ester (7.3 g) and benzyl chloride (6.2 g) was heated in a sealed tube at 140° for four hours. By fractionation of the products, a fraction (4 g) of b.p. 168-193°/3-4 mm was obtained. On standing, it yielded colorless crystals, which, after recrystallization from benzene, melted at 120-121°. They were colorless needles, soluble in benzene and in alcohol, poorly soluble in ether and in ligroin.

Found %: P 13.97
$C_{11}H_{15}O_3P$. Calculated %: P 13.71

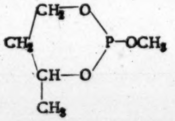
Rast molecular weight estimation: M (found) 231.1 (calculated for $C_{11}H_{15}O_3P$: 226.14).

3. Action of benzyl bromide on



Butyl 1-methyltrimethylene phosphite (2.6 g) and benzyl bromide (2.4 g) were heated in a sealed tube at 150-155° for four hours. When the tube was opened there was no odor of the original ester or of benzyl bromide. After standing overnight, the product partly crystallized out. The crystals (0.6 g, 21%) melted, after recrystallization from benzene, at 120-120.5°. In admixture with the preceding product it melted without depression.

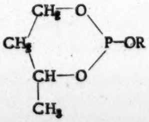
11. Action of Acetyl Bromide on



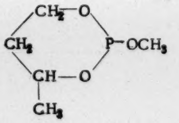
An ethereal solution of acetyl bromide (3.5 g) was added dropwise to a solution of methyl 1-methyltrimethylene phosphite (4.1 g) in dry ether (5 ml) contained in a small Arbuzov flask, which was cooled with snow. The temperature within the mixture did not exceed 8°. Solvent was driven off, and the reaction products were vacuum-distilled. A fraction (2.3 g, 47.3%) was isolated having b.p. 142-143° at 3-3.5 mm; d_4^{20} 1.2574; n_D^{20} 1.4555; found MR_D 38.20; calculated MR_D 38.10. It was an oily liquid having a faint odor. It dissolved in organic solvents and in water.

Found %: P 17.04
$C_6H_{11}O_4P$. Calculated %: P 17.40

12. Action of Water on the Ester



1. Action of Water on

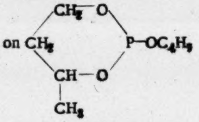


To 5.6 g of the methyl ester 0.67 g (one mole per mole of ester) of water was added (the water was slightly acidified with hydrochloric acid). The temperature of the mixture rose immediately to 97°. Vacuum fractionation yielded a fraction (2 g, 40%) of b.p. 150-155°/10-11 mm, and this rapidly crystallized out. The product was recrystallized from gasoline (m.p. 48-50°).

Found %: C 35.00; H 6.89; P 22.7

$C_4H_9O_3P$. Calculated %: C 35.27; H 6.66; P 27.79

2. Action of water on



Slightly acidified water (0.36 g) was added to butyl 1-methyltrimethylene phosphite (3.84 g). Reaction did not begin at once: at first an emulsion was formed, and the ester did not appear to react. After some time the mixture was warmed, and a clear homogeneous solution was formed. In the distillation of the products butyl alcohol was detected. Crystals of a cyclic acid, m.p. 48-50°, were obtained. The silver salt (decomposition temperature 220°) was prepared:

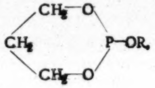
Found %: Ag 44.66

$C_4H_8O_3PAg$. Calculated %: Ag 44.40

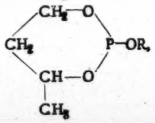
SUMMARY

1. By the action of 1,3-propanediol and of 1,3-butanediol on phosphorus trichloride, the cyclic compounds, trimethylene phosphorochloridite and 1-methyltrimethylene phosphorochloridite, have been prepared.

2. By reaction of the phosphorochloridites with alcohols in presence of dimethylaniline, the following mixed esters have been synthesized:



where R = CH_3, C_3H_7;



where R = CH_3, C_2H_5, C_3H_7.

Some of their properties have been studied.

LITERATURE CITED

[1] A. E. Arbuzov and V. M. Zoroastrova, Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci., No. 5, 770 (1952).*

Received June 23, 1952

A. M. Butlerov Chemical Research Institute
of the V.I. Ulyanov-Lenin Kazan State University

---

* See Consultants Bureau translation, p.697.

N-SUBSTITUTED CYCLIC ESTERS OF PHOSPHORAMIDOUS ACID

A. E. Arbuzov and V. M. Zoroastrova

The present work represents a development of our investigations of cyclic esters of phosphorous acid. We found in 1946 [1] that phosphorous trichloride reacts with glycols in presence of pyridine or dimethylaniline with formation of cyclic esters of phosphorochloridous acid. In this way we have synthesized, in the last few years, esters of phosphorochloridous acid having five-, six-, seven-, and eight-membered rings derived from α-, β-, and γ-glycols, and from diethylene glycol [2]. The phosphorochloridites are colorless fuming liquids, and are very reactive. Those having seven- and eight-membered rings ignite spontaneously in air and burn with a blue flame; they tend to polymerize. The phosphorochloridites react with anhydrous alcohols in presence of dimethylaniline or pyridine, giving mixed cyclic esters of phosphorous acid, which also are very reactive compounds having interesting characteristics.

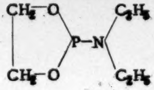
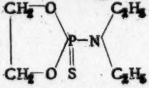
In the present work we have studied the reactions of phosphorochloridites derived from α- and β-glycols with certain aliphatic and aromatic amines: dimethylamine, diethylamine, piperidine, aniline, and methylaniline.

By the action of these amines on the phosphorochloridites, we have synthesized a number of N-substituted cyclic esters of phosphoramidous acid, which contain tervalent nitrogen as well as tervalent phosphorus. The physical properties of the compounds obtained are presented in Table 1.

The first seven compounds listed in Table 1 were prepared by introducing 1 mole of cyclic phosphorochloridite into an ether or benzene solution of 2 moles of amine*. The hydrogen chloride formed was taken up by the second molecule of amine and was separated from the reaction product as amine hydrochloride. The solvent was driven off, and the product was vacuum-distilled. Yields of N-substituted cyclic esters of phosphoramidous acid varied from 55 to 73%. The seven compounds are all colorless liquids, similar in appearance to the previously studied mixed cyclic esters of phosphorous acid, and having a faint but characteristic odor.

Compounds 8 and 9, which have aromatic radicals on the nitrogen, are very viscous liquids, also having characteristic odors. They were prepared by the action of aromatic amines on the phosphorochloridite in presence of metallic sodium. Yields did not exceed 22.8%.

All the synthesized N-substituted cyclic esters of phosphoramidous acid, like the full esters of phosphorous acid, react with cuprous halides. In this case also, the reaction proceeds with considerable evolution of heat. Some of the compounds formed with cuprous chloride, with cuprous bromide, and with cuprous iodide were prepared in a crystalline form (Table 2).

N-substituted cyclic esters of phosphoramidous acid are able to unite with sulfur. By the action of sulfur on , a product (b.p. 133-134.5° at 3 mm; d_4^{20} 1.1825, n_D^{20} 1.5050), was isolated in a pure form; it corresponded in analysis to .

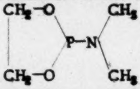
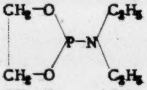
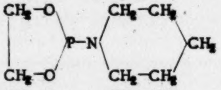
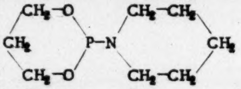
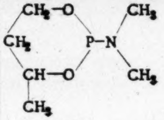
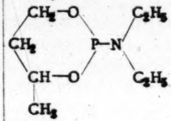
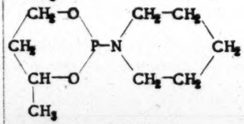
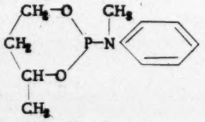
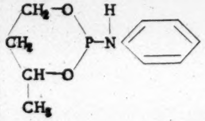
The products of the reaction of other N-substituted phosphoramidites with sulfur could not be obtained in a pure state since they were largely decomposed when distilled.

Alkyl halides also react with the nitrogen-containing esters, but the reaction is complex, and we did not

---

* After we had finished our investigation, there appeared a paper by H. J. Lucas, F. W. Mitchell, and C. N. Scully, "Cyclic Phosphites of some Aliphatic Glycols" (J. Am. Chem. Soc., 72, 5491 (1950), in which Compounds 2 and 3 (Table 1) are described. The value of MR_D for Compound 3 is given incorrectly in this paper.

TABLE 1

No.	Formula	B.p.	Pressure	d_0^{20}	n_D^{20}	MR_D	
		(°C)	(mm Hg)			Found	Calculated
1		61-62	11	1.1285	1.4730	33.58	33.88
2		66-67	3.5	1.0639	1.4680	42.61	43.08
3		89-90	2.5-3	1.1454	1.5040	45.27	45.49
4		96-97	4	1.1173	1.5020	50.01	50.16
5		71	13.5	1.0423	1.4650	43.26	43.12
6		69-70	2	1.0050	1.4620	52.36	52.38
7		95-96	3	1.0741	1.4930	54.95	54.77
8		133-134	3	1.1382	1.5442	62.65	62.60
9		136-137	2	1.1748	1.5558	57.84	57.93

succeed in isolating any homogeneous substances from the mixture of products. It is probable that the reaction results in rupture of the P—N link.

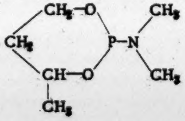
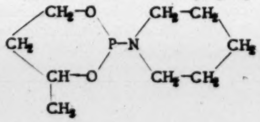
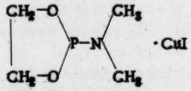
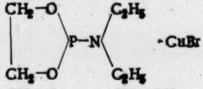
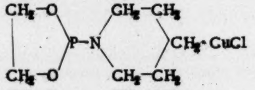
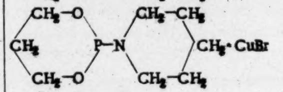
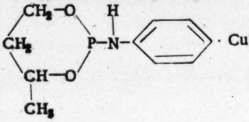
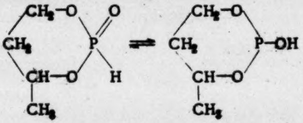
By the action of water (slightly acidified with hydrochloric acid) on the compounds  and 

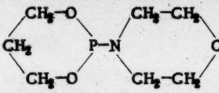
TABLE 2

No.	Formula	M.p. (°C)
1		108-109
2		108
3		128-130
4		167-167.5
5		134-138

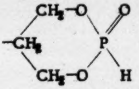
we isolated, in a pure state, the cyclic acid



(m.p. 48-50°), which was previously obtained by us by the hydrolysis of mixed cyclic esters; by the action of acidified water on

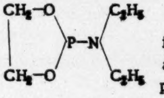


, we obtained



in a less pure form.

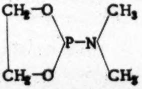
By the action of hydrogen on a solution of



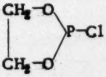
in ether we obtained a product that corresponded in analysis to the product of the addition of one atom of oxygen to one molecule of ethylene N,N-diethylphosphoramidite. The structure of this oxidation product was not investigated further.

EXPERIMENTAL

1. Preparation of the Ester



Dimethylamine (13 g) and dry benzene (150 ml) were placed in a flask fitted with reflux condenser and mechanical stirrer. The flask was cooled externally with water containing snow. The phosphorochloridite



(15 g), diluted with dry benzene (20 ml), was added from a dropping funnel. When reaction was complete, the precipitate of dimethylamine hydrochloride was filtered off and washed two or three times with dry benzene. The filtrate was vacuum-fractionated from an Arbuzov flask. After two fractionations, the following fractions were separated:

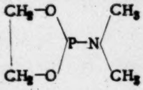
Fraction I, B.p. 60 - 61° at 12 mm; 1.2 g; n_D^{20} 1.4735
Fraction II, B.p. 61 - 62° at 11 mm; 11.6 g (yield 73%); n_D^{20} 1.4730
Fraction III, B.p. 62 - 63.5° at 11 mm; 0.5 g; n_D^{20} 1.4728

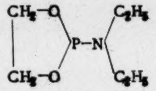
Fraction II was investigated in greater detail: d_4^{20} 1,1285; d_0^0 1.1487; n_D^{20} 1.4730. Found MR_D 33.58; calculated MR_D 33.88.

Found %: P 22.84; N 10.61
$C_4H_{10}O_2PN$. Calculated %: P 22.94; N 10.36

Fraction II was a mobile oily liquid having an unpleasant odor reminiscent of the odor of trimethyl phosphite. It was soluble in ether, benzene, chloroform, and other organic solvents; it reacted vigorously with water; and with cuprous halides it gave crystalline complex compounds, which decomposed rapidly in air. Thus, when CuCl (0.5 g) was added to the ester (0.75 g), the temperature of the mixture rose to 49° and the whole mass rapidly crystallized. However, when attempts were made to recrystallize the product from benzene, it decomposed. By reaction in a similar way of equimolecular proportions of ester and cuprous iodide, a product of m.p. 108-109° (from butyl acetate) was obtained. Analysis for iodine gave the following results:

Found %: I 38.81
$C_4H_{10}O_2PNCuI$. Calculated %: I 38.98

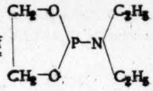
Reaction of  **with methyl iodide.** Methyl iodide (7.1 g) was added to the ester (6.6 g, i.e., one mole per mole of methyl iodide). The mixture immediately became milky, and its temperature rose to 103° and higher. The contents of the tube started to boil, and the greater part of them were ejected. The remaining part consisted of a thick red mass, and attempts to isolate definite products from this by vacuum distillation were not successful.

2. Preparation of the Ester 

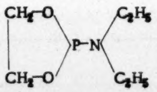
The materials taken for reaction were: ethylene phosphorochloridite (35.44 g), diethylamine (41 g), and dry ether (200 ml). The phosphorochloridite, diluted with an equal amount of ether, was added dropwise to the mechanically stirred ethereal solution of the amine. When reaction was complete, the reaction mixture was heated on a water bath for one hour. After the usual treatment, the reaction products were vacuum-distilled from an Arbuzov flask. After three distillations a product (30 g, 65.9%) having b.p. 66-67°/3.5 mm, d_0^{20} 1.0639; n_D^{20} 1.4680; found MR_D 42.61; calculated MR_D 43.08, was obtained.

Found %: P 19.33; 19.23; N 8.77
$C_6H_{14}O_2PN$. Calculated %: P 19.00; N 8.58

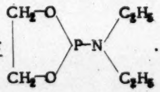
It was a colorless oil of characteristic odor. Oxidation of this or the preceding ester with nitric acid was accompanied by deflagration.

Reaction of  **with CuCl and with CuBr.** 1) When the ester (1.63 g) and cuprous chloride (0.99 g) were mixed, the temperature rose to 53°. A thick mass, soluble in ether, benzene and chloroform, was formed; attempts to crystallize it failed. 2) The ester (0.81 g) and CuBr (0.71 g) yielded a colorless crystalline substance, which, after two crystallizations from benzene-gasoline, melted at 108°. It was unstable in air.

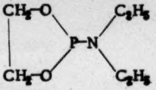
Found %: Br 25.73; P 10.33
$C_6H_{14}O_2PNCuBr$. Calculated %: Br 26.06; P 10.11

Addition of sulfur to the ester  . Finely divided crystalline sulfur (1 g) was added to the cooled ester (5 g, i.e. one mole per mole of sulfur), contained in a small Arbuzov flask. A highly exothermic reaction occurred, and the sulfur dissolved in the ester with formation of a homogeneous colorless solution. The solution was vacuum-distilled yielding a product (3 g) of b.p. 133-134.5°/3 mm (with some decomposition) (d_0^{20} 1.1825; n_D^{20} 1.5050; found MR_D 48.92; calculated MR_D 48.51.) It was a viscous liquid of faint odor.

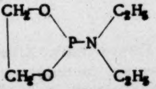
Found %: P 16.14; S 16.92
$C_6H_{14}O_2PNS$. Calculated %: P 15.83; S 16.43

Action of C_2H_5I on the ester  . A mixture of the ester (10.62 g) and ethyl iodide (10.2 g, i.e., one mole per mole of ester) was allowed to stand in a sealed tube at room temperature for five days. When the tube was opened, there was no odor of the original ester. The contents consisted of a fairly thick, colorless liquid. By distillation at ordinary pressure on the water bath, 5 g of ethyl iodide was driven off. When the mixture was heated more strongly, a very vigorous reaction set in with evolution of gaseous products; it lasted for 2-3 minutes. The contents of the flask became dark red. A small amount of dark-red liquid was driven off at 110-112° under 2.5-5.5 mm pressure, and a large residue of viscous liquid remained in the flask. The experiment was repeated several times, always with the same result: it was not found possible to isolate any product in the pure state.

Action of hydrogen peroxide on



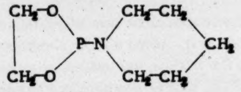
. To a solution of hydrogen peroxide (2.5 g of 100%) in dry ether (100 ml),



(10 g) was added in three portions, the reaction flask being cooled with snow. With the addition of each portion of the ester, a vigorous reaction occurred and the reaction mixture boiled. The reaction products were distilled, and a fraction (4.2 g, 38.5%) of b.p. 132°/5.5-6 mm was separated. It was a colorless odorless liquid, soluble in organic solvents and in water and having the following constants: d_4^{20} 1.1735; n_D^{20} 1.4522; calculated MR_D 41.95; found MR_D 41.18.

Found %: P 17.27
$C_6H_{14}O_3PN$. Calculated %: P 17.30

3. Preparation of the ester



The phosphorochloridite (20 g) was added to a mechanically stirred solution of piperidine (27 g) in ether (100 ml). The mixture was heated for one hour on the water bath and was then cooled to room temperature. The precipitate of piperidine hydrochloride was filtered off, and the filtrate was vacuum-distilled twice. A product (19 g, 68.5%) was obtained that boiled at 89-90° under 2.5-3 mm pressure and had d_4^{20} 1.1454; n_D^{20} 1.5040; found MR_D 45.27; calculated MR_D 45.49.

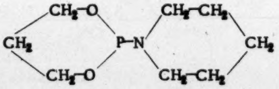
Found %: P 17.53; N 8.16
$C_7H_{14}O_2PN$. Calculated %: P 17.70; N 7.99

The product was more viscous than the previous esters.

Compound with cuprous chloride. By reaction in equimolecular proportions of the ester with CuCl, a crystalline substance was obtained. It was recrystallized several times from benzene-gasoline (m.p. 128-130°). The crystals were colorless, but rapidly yellowed in air.

Found %: Cl 12.79
$C_7H_{14}O_2PNCuCl$. Calculated %: Cl 12.92

4. Preparation of the Ester



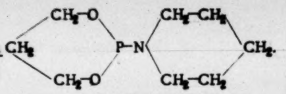
The phosphorochloridite, diluted with an equal volume of dry ether, was added to a mechanically stirred solution of piperidine (20 g) in dry ether (120 ml). As soon as the first drops of phosphorochloridite had been added, a white crystalline precipitate of piperidine hydrochloride began to appear. When the whole of the phosphorochloridite had been added, the reaction mixture was heated on the water bath for 30 minutes. Vacuum distillation yielded a product (14 g, 65%) of b.p. 96-97°/4 mm, d_4^{20} 1.1173; n_D^{20} 1.5020; found MR_D 50.01; calculated MR_D 50.11; a colorless oil having an odor similar to that of the preceding piperidine compound.

Found %: N 7.8
$C_8H_{16}O_2PN$. Calculated %: N 7.4

Compound with cuprous bromide. CuBr (0.71 g) was added to the ester (0.95 g). The temperature of the mixture rose to 78°, and a homogeneous mass was formed which rapidly crystallized. The product, after recrystallization from butyl acetate, formed colorless glistening crystals, m.p. 167-167.5°.

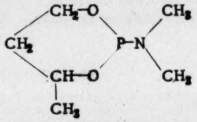
Found %: Br 24.05
$C_8H_{16}O_2PNCuBr$. Calculated %: Br 24.02

Action of water on



. Water (0.66 g), slightly acidified with hydrochloric acid, was added to an equimolecular proportion of the ester (7 g), contained in a small Arbuzov flask. After some time, the emulsion that was at first formed was converted into a homogeneous solution, and the temperature rose to 46°. Vacuum distillation yielded a fraction of b.p. 143-144°/4 mm; n_D^{20} 1.4658.; a colorless, very viscous liquid, soluble in water, alcohol, benzene, and dioxane, but not soluble in ether.

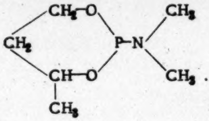
5. Preparation of the Ester



1-Methyltrimethylene phosphorochloridite was added to a cooled, mechanically stirred solution of dimethylamine (11 g) in dry ether (120 ml). When all the phosphorochloridite had been added, dimethylamine hydrochloride was filtered off, and the filtrate was vacuum-distilled from an Arbuzov flask having two bulbs. After redistillation, a product (11.51 g, 57.8%) was obtained having b.p. 71° at 13.5 mm; d_4^{20} 1.0423; n_D^{20} 1.4650; found MR_D 43.26; calculated MR_D 43.12.

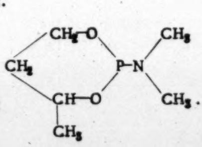
Found %: P 19.00
$C_6H_{14}O_2PN$. Calculated %: P 19.00

Action of methyl iodide on



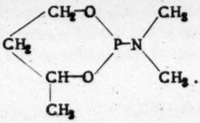
. Methyl iodide (3.6 g) was added to the ester (4.2 g), which was cooled with snow. A very violent reaction occurred, and a part of the mixture was thrown out of the reaction flask. A viscous liquid was obtained. Vacuum distillation yielded 3-4 drops of a fraction of b.p. 57-62°/3 mm. The residue did not distil (bath temperature 200-220°); it was a thick greasy liquid of unpleasant odor.

Action of $C_6H_5CH_2Br$ on

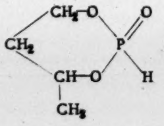


. The ester (2 g) was mixed with benzyl bromide (2.08 g). The temperature of the mixture rose very slowly and remained at 30-36° for 30 minutes. The whole of the benzyl bromide reacted. The reaction products were allowed to stand for two hours at room temperature and then were vacuum-distilled. A fraction (1.1 g) of b.p. 73-112°/3 mm was obtained (bath temperature 220°). The remaining part (1.8 g) was a solid glasslike product, insoluble in organic solvents and in water.

Action of water on

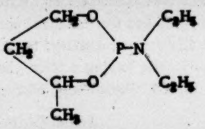


. Water, (0.36 g) slightly acidified with hydrochloric acid, was added to the ester (3 g), contained in a small Arbuzov flask. On being shaken, the mixture at first formed an emulsion, and then reaction set in with rise in temperature to 45° and the appearance of the odor of dimethylamine. Distillation yielded a product (1 g) of b.p. 138°/3.5 mm, which crystallized when seeded with crystals of the previously prepared cyclic acid:



; m.p. 48-49°.

6. Preparation of the Ester

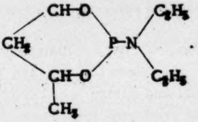


This compound was obtained in analogous fashion from 1-methyltrimethylene phosphorochloridite (18.7 g) and diethylamine (17.7 g) in a medium of dry ether. After the usual treatment of the reaction products and two vacuum fractionations, a fraction (12.8 g, 55.3%) was obtained having b.p. 69-70°/2 mm; d_4^{20} 1.0050; n_D^{20} 1.4625; found MR_D 52.38; calculated MR_D 52.36.

Found %: P 16.21; 16.10; N 7.56

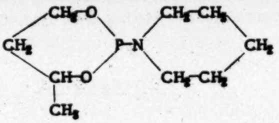
$C_8H_{18}O_2PN$. Calculated %: P 16.21; N 7.32

Action of ethyl bromide on



A mixture of the ester (8.8 g) and ethyl bromide (5 g) was heated in a sealed tube having a drawn-out portion. Heating was at 50-55° for six hours, at 70-80° for four hours, and at 90° for three hours. No further change in volume was then observed. On being vacuum-distilled, the reaction products were largely decomposed; it was not possible to isolate any individual substances.

7. Preparation of the Ester

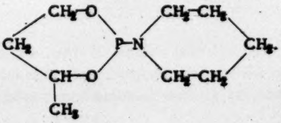


The phosphorochloridite (25.6 g), diluted with an equal amount of ether, was added to a mechanically stirred solution of piperidine (28.17 g) in dry ether (100 ml), contained in a flask fitted with reflux condenser. The reaction product was vacuum-distilled from an Arbuzov flask, and after a second distillation a liquid (20 g, 59.5%) was obtained of b.p. 95-96°/3 mm, d_4^{20} 1.0741; n_D^{20} 1.4930; found MR_D 54.95; calculated MR_D 54.77.

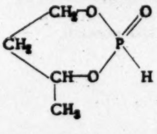
Found %: P 15.43; N 6.47

$C_9H_{18}O_2PN$. Calculated %: P 15.26; N 6.89

Action of water on

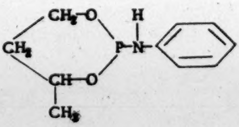


Water (0.44 g), slightly acidified with hydrochloric acid, was added dropwise to the ester (5 g). The emulsion formed turned rapidly into a homogeneous solution with rise in temperature to 40°. By vacuum distillation, a substance (2 g) of b.p. 133-134°/4 mm was isolated. By introduction of a few crystals of the previously prepared acid



, it crystallized (m.p. 48-50°). Similar crystals were separated from the residue in the distillation flask.

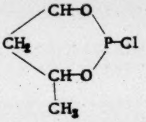
8. Synthesis of



1-Methyltrimethylene phosphorochloridite (21.5 g) was added dropwise to a mixture of aniline (12.94 g), sodium dust (3.2 g), and dry xylene (60 ml). The reaction was accompanied by evolution of heat. When the whole of the phosphorochloridite had been added, the reaction mixture was heated on the water bath with stirring [illegible] one hour. The mixture was cooled, and the colloidal precipitate of sodium chloride and the unchanged sodium were filtered off. The filtrate was distilled twice, giving a product (3 g, 22.8%) of b.p. 136-137°/12 mm; a colorless, very viscous liquid, having a faint but characteristic odor. It was soluble in organic solvents and had d_4^{20} 1.1748; n_D^{20} 1.5558. Found MR_D 57.84; calculated MR_D 57.93.

Found %: P 14.75; N 6.49
$C_{10}H_{14}O_2PN$. Calculated %: P 14.73; N 6.63

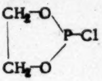
It yielded by reaction with CuI a crystalline product having m.p. 134-138° (from benzene-ligroin).

9. Reaction of  with Methylaniline

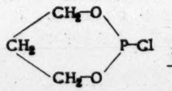
The reaction was carried out as in the preceding section, the materials taken being: methylaniline (10.7 g), metallic sodium in the form of dust (2.3 g), dry xylene (50 ml), and 1-methyltrimethylene phosphorochloridite (12.64 g). A product (5.1 g, 22.6%) was obtained having b.p. 133-134° at 3 mm; d_4^{20} 1.1382; n_D^{20} 1.5442; found MR_D 62.65; calculated MR_D 62.60.

Found %: P 14.03; N 6.42
$C_{11}H_{16}O_2PN$. Calculated %: P 13.77; N 6.22

The product, like the preceding compound, reacts with cuprous chloride and cuprous iodide with rise of temperature. Attempts to isolate the complexes in crystalline form were not successful.

10. Reaction of  with $(C_6H_5)_3CNH_2$

$(C_6H_5)_3CNH_2$ (0.5 g) and ethylene phosphorochloridite (0.25 g) were heated together in dry benzene (5 ml). A precipitate (0.3 g) quickly appeared; the product, after being washed with benzene, melted at 242-246°. The melting point and analytical figures for chlorine (found: Cl 11.19%: calculated Cl 11.99%) corresponded to triphenylmethylamine hydrochloride. It was not found possible to isolate any other product.

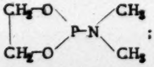
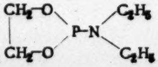
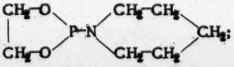
11. Reaction of  with Butylamine

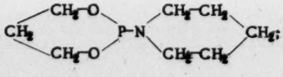
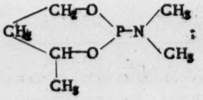
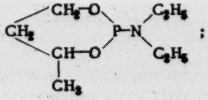
Trimethylene phosphorochloridite, diluted with an equal volume of ether, was added to a solution of butylamine (20 g) in dry ether (180 ml). When the whole of the phosphorochloridite had been added, the mixture was heated on the water bath for 30 minutes. By vacuum fractionation, a substance (3 g) boiling over a wide range of temperature (123-154°/4 mm) with decomposition was separated. A second fractionation was carried out, but again no individual substances were isolated.

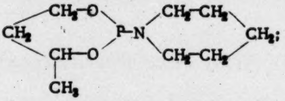
SUMMARY

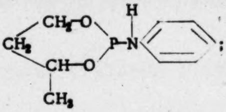
1. It has been found that cyclic esters of phosphorochloridous acid react with aliphatic and aromatic amines, forming N-substituted cyclic esters of phosphoramidous acid.

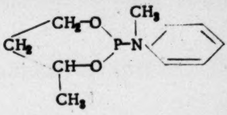
2. The following compounds have been synthesized:

1)  ; 2)  ; 3) 

4)  5)  6) 

7) 

8) 

9) 

and some of their properties have been studied.

Received June 23, 1952

A. M. Butlerov Chemical Research Institute
of the V. I. Ulyanov-Lenin Kazan State University

LITERATURE CITED

[1] A. E. Arbuzov, Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 2, 226 (1946).

[2] A. E. Arbuzov, V. M. Zoroastrova, and N. I. Rizpolozhensky, Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 2, 208 (1949); A. E. Arbuzov and M. M. Azanovskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 5, 473 (1949); A. E. Arbuzov and V. M. Zoroastrova, Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 4, 357 (1950); A. E. Arbuzov and V. M. Zoroastrova, Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 5, 536 (1951).

BLANK
PAGE

PHOSPHOROUS ACID DERIVATIVES CONTAINING A CYCLOHEXYL RADICAL

A. E. Arbuzov and F. G. Valitova

Cyclohexyl derivatives of phosphorous acid have received little study. In 1949 the English chemists Cook, Hett, and others [1] described a method for preparing dicyclohexylphosphorous acid (i.e., dicyclohexyl hydrogen phosphite and/or dicyclohexyl phosphonate), in a yield of 60 - 65% by the action of cyclohexanol on phosphorus trichloride in carbon tetrachloride. No constants other than the boiling point, 135-143°/0.6-1 mm, were cited by the authors. When we attempted to prepare dicyclohexylphosphorous acid by the method of the English chemists, we always obtained a negative result, for at some time during the distillation of the reaction products the contents of the flask always foamed up and then decomposed completely. Repeat experiments invariably resulted in decomposition of the reaction products, and the nature of the conditions necessary for a satisfactory result is not clear*.

Since then we have succeeded in finding a reliable method for preparing dicyclohexylphosphorous acid: by the action of cyclohexanol on phosphorus trichloride (molar ratio 3:1) in presence of pyridine in dry ether. From this reaction two substances were isolated: dicyclohexylphosphorous acid (30% yield) and a small amount of tricyclohexyl phosphite.

Dicyclohexylphosphorous acid is a colorless mobile liquid of characteristic odor having the following constants: b.p. 149-150°/1 mm; d_0^{20} 1.0982; n_D^{20} 1.4800. In ether solution it reacts with metallic sodium forming an ether-soluble salt similar to sodium diethylphosphite. When an ethereal solution of bromotriphenylmethane is added to the ethereal solution of the salt, there appears very rapidly a golden-yellow coloration, characteristic for the triphenylmethyl free radical [2].

By a change in the molecular proportions of cyclohexanol, phosphorus trichloride, and pyridine, it was found possible to go over to the preparation of dicyclohexyl phosphorochloridite. In this case the reaction may be expressed by the equation:

$$2C_6H_{11}OH + PCl_3 + 2C_5H_5N \longrightarrow (C_6H_{11}O)_2PCl + 2C_5H_5N{\cdot}HCl.$$

When the reaction products are distilled, a readily volatile, somewhat turbid liquid first comes over, and then comes the expected phosphorochloridite. Almost immediately after this has passed over, the contents of the flask foam up and decompose completely. The phosphorochloridite, which is obtained in 40-45% yield, is a colorless, mobile liquid that fumes slightly in air; it has b.p. 152-153°/1 mm; d_0^{20} 1.0811; n_D^{20} 1.4852.

The readily accessible method described above for the preparation of the phosphorochloridite made it possible for us to prepare tricyclohexyl phosphite and a number of other, mixed esters. Starting from the phosphorochloridite we obtained tricyclohexyl phosphite by three methods: 1) by the action of cyclohexanol in presence of pyridine, 2) by the action of cyclohexanol in presence of dimethylaniline, and 3) by the action of the sodium derivative of cyclohexanol (sodium cyclohexyloxide). All the reactions were carried out in a medium of anhydrous ether. The best result was obtained by the action on the phosphorochloridite of sodium cyclohexyloxide, when the yield reached a value of 60-65%.

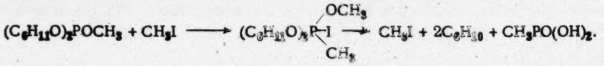
Tricyclohexyl phosphite, immediately after being distilled, was a colorless viscous liquid of b.p. 175-176° at 1 mm, but after some time the whole of the liquid in the receiver solidified to a mass of clear crystals that tended to stick to one another. When the crystals were removed from the flask and exposed to air, they rapidly became liquid, and to determine their approximate melting point, therefore, a thermometer was inserted into the mass of crystals in the flask: the whole of the contents of the flask was found to melt within the range 60-75°.

By treatment with cuprous bromide, tricyclohexyl phosphite yielded a copper compound that crystallized well from alcohol and melted at 173-174°. We further prepared, by the action of alkoxides on dicyclohexyl phosphorochloridite in a medium of dry ether, a number of mixed esters of formula $(C_6H_{11}O)_2POAlk$, where $Alk = CH_3$, C_2H_5, C_4H_9, $C_6H_5CH_2$. Boiling points and other constants of the esters obtained are given later in a table.

---

* B. A. Arbuzov (private communication) succeeded on one occasion only in preparing dicyclohexylphosphorous acid in good yield (about 60%) by the method of the English chemists.

All the mixed esters obtained were found to react with cuprous bromide with slight evolution of heat (30-40°), forming viscous liquids, which we did not succeed in crystallizing. The "isomerization" reaction carried out on these alkyl dicyclohexyl phosphites proceeded in an extremely peculiar fashion. Thus, when dicyclohexyl methyl phosphite was heated with methyl iodide in a closed tube at 200°, instead of the diminution in the volume of the reaction mixture which is usually observed in these cases, an increase in volume occurred. When the contents of the tube were heated further to 210-220°, the previously homogeneous liquid formed into two layers, the upper and thicker layer being an almost colorless, mobile liquid, and the lower layer being a slightly yellowish, viscous liquid. The tube was opened, and the upper layer was carefully poured off into a small flask and distilled. The greater part of the liquid that came over had a boiling point close to that of cyclohexene; it had the odor of cyclohexene. The tube was cut off almost at the level of the liquid in the lower layer, and the latter was poured off into a small dish, which was placed in a desiccator; the desiccator was evacuated with a water pump. After one day the contents of the dish had crystallized out almost completely. Examination of this substance showed it to be methylphosphonic acid, and here it should be remembered that preparation of methylphosphonic acid in a crystalline form presents a problem that is far from easy. This interesting reaction may be represented by the following equation:



$$(C_6H_{11}O)_2POCH_3 + CH_3I \longrightarrow (C_6H_{11}O)_2\overset{OCH_3}{\underset{CH_3}{P}}-I \longrightarrow CH_3I + 2C_6H_{10} + CH_3PO(OH)_2.$$

The behavior we have described for dicyclohexyl methyl phosphite is characteristic of that observed in the isomerization reaction carried out on the remainder of the mixed esters (and also tricyclohexyl phosphite) that we have prepared: in all cases there was a small increase in the volume of the reaction mixture when heated to 200°, and then, with rise in temperature to 220°, separation into two layers occurred. The upper layer, independently of the identity of the alkyl radical of the mixed ester, came over mainly in the boiling range of cyclohexene. The lower layer, by analogy with that obtained in the methyl ester experiment, should have contained the corresponding alkylphosphonic acid, but we have not yet succeeded in obtaining the supposed alkylphosphonic acids in a crystalline form. We have not lost hope of doing this in the future by carrying out experiments with greater amounts of starting materials.

In addition to the esters described above, we have prepared yet another mixed ester containing a cyclohexyl group, starting from o-phenylene phosphorochloridite, which we described in a previous communication [3]. By the action of cyclohexanol on o-phenylene phosphorochloridite in presence of pyridine, cyclohexyl-o-phenylene phosphite was obtained in 62% yield. Constants of the ester are given in the table. This ester, unlike the alkyl dicyclohexyl phosphites, gives a well crystallizing copper compound with cuprous bromide (m.p. 137-138°). The crystals of the copper compound are unstable both in air and in a sealed tube: they turn green fairly rapidly, and then turn black. In the isomerization reaction with cyclohexyl iodide or bromide, cyclohexyl o-phenylene phosphite behaves differently from the other mixed esters. When the reactants are heated in a sealed tube to 210°, no appreciable change in volume is to be observed; at temperatures above 210°, decomposition sets in.

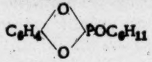
Tricyclohexyl phosphite and cyclohexyl o-phenylene phosphite were taken as examples for the study of the action of bromotriphenylmethane at 180° in sealed tubes. The viscous yellowish masses that were obtained were hydrolyzed by heating with 10% hydrochloric acid in sealed tubes, and in both cases a resinous mass was precipitated, from which, by treatment with alcohol and repeated recrystallization, it was found possible to isolate triphenylmethylphosphonic acid, m.p. 277-278°. By the action of bromotriphenylmethane on dicyclohexyl ethyl phosphite we obtained, unexpectedly, crystals of triphenylmethane, m.p. 92°.

EXPERIMENTAL

Preparation of Dicyclohexylphosphorous Acid $(C_6H_{11}O)_2POH$

An ethereal solution of phosphorus trichloride (22.9 g) was added gradually under stirring to a solution of cyclohexanol (50 g) and pyridine (39.5 g) in dry ether (50 ml). Reaction proceeded with evolution of heat and was continued for three hours. The supernatant ether layer was poured from the precipitate that had formed into a distillation flask. The precipitate was washed with ether by decantation, and the washings were poured into

TABLE 1

No.	Formula	B.p. °C/1 mm	d_0^{20}	n_D^{20}	MR_D found	MR_D calculated	Phosphorus content found	Phosphorus content calculated	Yield %
1	$(C_6H_{11}O)_2POH$	149-150	1.0982	1.4800	63.65	63.57	12.22; 12.37	12.60	39
2	$(C_6H_{11}O)_2PCl$	152-153	1.0811	1.4852	70.11	69.92	11.54; 12.02	11.72	45
3	$(C_6H_{11}O)_3P$	175-176	–	–	–	–	9.30; 9.62	9.45	63
4	$(C_6H_{11}O)_2POCH_3$	127-128	1.0491	1.4750	–	–	12.14; 12.10	11.92	41
5	$(C_6H_{11}O)_2POC_2H_5$	129-130	1.0298	1.4730	75.91	75.52	11.45; 11.57	11.31	33
6	$(C_6H_{11}O)_2POC_4H_9$	139-140	0.9827	1.4618	84.47	84.75	10.52; 10.24	10.26	30.7
7	$(C_6H_{11}O)_2PO{-}CH_2{-}C_6H_5$	193-195	1.0594	1.5088	94.65	95.06	9.23; 9.47	9.22	43
8	 $C_6H_4O_2POC_6H_{11}$	125-126	1.1661	1.5270	62.76	62.68	12.86; 13.00	13.02	62

the flask. The ether was removed, and the residue was distilled under 1 mm pressure. The following fractions were obtained

Fraction I, b.p. 60-150°; 5 g; n_D^{20} 1.4802

Fraction II, b.p. 150-160°; 19 g; d_0^{20} 1.4812

Fraction III, b.p. 166-179°; 5 g - crystallized out

Fractions II and III were redistilled, yielding a fraction (16 g, 39%) of b.p. 149-150°; n_D^{20} 1.4800; d_0^{20} 1.0982; found MR_D 63.65; calculated MR_D 63.57.

Found %: P 12.22, 12.37
$C_{12}H_{23}O_3P$. Calculated %: P 12.60

Preparation of Dicyclohexyl phosphorochloridite $(C_6H_{11}O)_2PCl$

An ethereal solution of phosphorus trichloride (69 g) was added under stirring to a solution of cyclohexanol (100 g) and pyridine (79 g) in ether. Reaction proceeded with evolution of heat, and it continued for four hours. On the next day the supernatent ether layer was poured off into a distillation flask, and ether washings decanted from the precipitate were added. The ether was removed, and the residue was distilled under a pressure of 1 mm. Two fractions were obtained: a turbid fraction, b.p. 152-153°, and a clear fraction, b.p. 140-160°; heating at above 160° led to decomposition. After two distillations a fraction (61 g, 45%) was obtained having b.p. 152-153°, n_D^{20} 1.4852; d_0^{20} 1.0811; found MR_D 70.11; calculated MR_D 69.92.

Found %: P 11.54; 12.02
$C_{12}H_{22}O_2P$. Calculated %: P 11.72
Found %: Cl 13.85; 13.62
$C_{12}H_{22}O_2PCl$. Calculated %: Cl 13.42;

Preparation of Tricyclohexyl Phosphite $(C_6H_{11}O)_3P$

1. In presence of pyridine. An ethereal solution of dicyclohexyl phosphorochloridite (31 g) was added slowly under stirring to an ethereal solution of cyclohexanol (11.7 g) and pyridine (9.2 g). When reaction was complete, the crystalline precipitate was rapidly filtered off and washed with dry ether. The filtrate was distilled to remove ether, and the residue was fractionated under a pressure of 1 mm. The following fractions were obtained:

Fraction I, b.p. 65-158°; 4.5 g

Fraction II, b.p. 158-168°; 11.5 g

Fraction III, b.p. 168-180°; 15.6 g

Further distillation of Fractions II and III yielded a fraction of b.p. 175-176°, which crystallized in the receiver (16 g, 41%).

Found %: P 9.30; 9.62
$C_{18}H_{33}O_3P$. Calculated %: P 9.45

2. In presence of dimethylaniline. An ethereal solution of the phosphorochloridite (10 g) was added to an ethereal solution of cyclohexanol (3.8 g) and dimethylaniline (4.5 g). The supernatent ethereal layer was poured off into a distilling flask, and the ether was distilled off. The residue was distilled under a pressure of 1 mm Hg, and the following fractions were isolated:

Fraction I, b.p. 50-150°; 1.3 g

Fraction II, b.p. 150-160°; 4.2 g

Fraction III, b.p. 160-180°; 5.5 g

A second distillation of Fraction III yielded a fraction (4 g, 32%), of b.p. 175-176°, which crystallized.

Action of the phosphorochloridite on sodium cyclohexyloxide. An ethereal solution of the phosphorochloridite (10 g) was added to an ethereal solution of sodium cyclohexyloxide prepared from metallic sodium (0.87 g) and cyclohexanol (3.8 g) by the "swelling" technique [4]. The precipitate present was filtered off, and the filtrate was distilled. The thick oil that remained after removal of ether distilled over at 175-176° and completely solidified. In this case there were no other fractions. The melting point of the crystals was determined with a thermometer placed in the flask. The substance melted completely in the range 60-75°. The yield of the ester was 7.8 g (63%).

Action of cuprous bromide on tricyclohexyl phosphite. Tricyclohexyl phosphite (1 g) and cuprous bromide (0.43 g) were introduced into a small flask. A thermometer placed in the mixture indicated a rise in temperature to 42°, after which no further rise occurred. The white mass formed was recrystallized twice from dry alcohol; it melted at 173-174°.

Found %: Br 9.75; 9.55
$C_{36}H_{66}O_6P_2CuBr$. Calculated %: Br 9.99

Preparation of Alkyl Dicyclohexyl Phosphites

Alkyl dicyclohexyl phosphites were prepared by the action in a dry ether medium of dicyclohexyl phosphorochloridite on sodium alkoxides. When reaction was complete, the ethereal solution was either filtered off from the precipitate that had formed, or separated by submitting the contents of the flask to centrifuging. The filtrate was fractionated (under reduced pressure when the ether had been removed).

1. Preparation of dicyclohexyl methyl phosphite. The materials taken for reaction were: the phosphorochloridite (13 g), methanol (1.6 g), and sodium (1.15 g). After removal of ether the residue was distilled at 1 mm, and the following fractions were obtained:

Fraction I, b.p. 60-120°
Fraction II, b.p. 120-140°

After two distillations a fraction (5.3 g, 41%) of b.p. 127-128° was obtained; it had n_D^{20} 1.4750; d_0^{20} 1.0491.

Found %: P 12.14; 12.10
$C_{13}H_{25}O_3P$. Calculated %: P 11.92

2. Preparation of dicyclohexyl ethyl phosphite. The phosphorochloridite (10 g) was added to sodium ethoxide prepared from sodium (0.85 g) and ethanol (1.7 g). Fractionation of the reaction products yielded the fractions:

Fraction I, b.p. 80-120°
Fraction II, b.p.120-135°

After a second distillation a fraction of b.p. 129-130°/1 mm (3.4 g, 33%) was isolated. It had n_D^{20} 1.4730; d_0^{20} 1.0298; found MR_D 75.91; calculated MR_D 75.52.

Found %: P 11.45; 11.57
$C_{14}H_{27}O_3P$. Calculated %: P 11.31

3. Preparation of butyl dicyclohexyl phosphite. An ethereal solution of the phosphorochloridite (10 g) was added to sodium butoxide prepared from sodium (0.81 g) and butyl alcohol (2.04 g). After distillation of the products of the reaction the following fractions were obtained:

Fraction I, b.p. 80-130°
Fraction II,b.p. 130-150°

After a second distillation a fraction (3.5 g, 30.7%) was obtained of b.p. 139-140°/1 mm and having n_D^{20} 1.4618; d_4^{20} 0.9827; found MR_D 84.47; calculated MR_D 84.75.

Found %: P 10.52; 10.24
$C_{16}H_{31}O_3P$. Calculated %: P 10.26

4. Preparation of benzyl dicyclohexyl phosphite. Sodium benzyloxide was prepared in this case not by the swelling technique, but by the action of benzyl alcohol (16 g) on sodium (3.45 g) in dry ether, heat being applied. To the solution obtained an ethereal solution of the phosphorochloridite (40 g) was added. When reaction was complete, the ether layer was distilled (under reduced pressure when the ether had been removed). The following fractions were obtained:

Fraction I, b.p. 80-160°
Fraction II, b.p. 160-200°

After a second distillation a fraction (22 g, 43%) of b.p. 193-195° was obtained; it had n_D^{20} 1.5088; d_4^{20} 1.0594; found MR_D 94.65; calculated MR_D 95.06.

Found %: P 9.23: 9.37
$C_{19}H_{29}O_3P$. Calculated %: P 9.22

5. Preparation of cyclohexyl o-phenylene phosphite. An ethereal solution of o-phenylene phosphorochloridite (20 g) was added under stirring to an ethereal solution of cyclohexanol (11.5 g) and pyridine (9.8 g). Reaction set in, heat being evolved. The supernatent ethereal layer was distilled, the oil that remained after removal of ether being distilled under 1 mm pressure. The following fractions were obtained:

Fraction I, b.p. 80-120°, 3 g
Fraction II, b.p. 120-130°; 18 g

A second distillation yielded a fraction (17 g, 62%) of b.p. 125-126°; it had n_D^{20} 1.5270; d_4^{20} 1.1661; found MR_D 62.76; calculated MR_D 62.68.

Found %: P 12.86; 13.00
$C_{12}H_{15}O_3P$. Calculated %: P 13.02

Action of cuprous bromide on cyclohexyl o-phenylene phosphite. Cuprous bromide (1.8 g) was introduced into a flask containing cyclohexyl o-phenylene phosphite (2 g). The temperature of the mixture rose to 45°. The white mass obtained was recrystallized twice from absolute alcohol, yielding crystals of m.p. 137-138°. Further recrystallization did not affect the melting point. After a day's exposure to the atmosphere the crystals turned green; they then began to blacken.

Found %: P 8.72; 8.49
$C_{12}H_{15}O_3PCuBr$. Calculated %: P 8.12

Attempted isomerization of dicyclohexyl methyl phosphite in presence of methyl iodide. A mixture of dicyclohexyl methyl phosphite (2.5 g) and methyl iodide (1.4 g) was heated in a sealed tube having a constriction for facilitating observation of volume change. On being heated to 200°, the liquid increased in volume. Between 200° and 215° two layers formed. The upper layer was carefully poured off into a small flask and was distilled under normal pressure. Two fractions were obtained: one of b.p. 40-80°, the boiling temperature of which rose rapidly (about one-third of the total); and one of b.p. 80-85° having an odor similar to that of cyclohexene.

The lower layer was poured onto a watch glass and left in a desiccator; it had solidified by the next day. The unpurified crystals melted at 98-100° (melting point of methylphosphonic acid, 103-104°).

Action of bromotriphenylmethane on cyclohexyl o-phenylene phosphite. A mixture of the ester (2 g) and bromotriphenylmethane (2.7 g) was heated in a sealed tube to 180°. A thick yellow liquid was formed. The contents of the tube were submitted to a hydrolysis treatment, 15% hydrochloric acid (10 ml) being added in the tube, which was heated at 200° for four hours. A resin came down, and the formation of crystals was noted in the aqueous layer. The resin was first purified by crystallization from benzene, and the resulting gray crystals were recrystallized from dry alcohol. The crystals obtained melted at 277-278°, the melting point of triphenylmethylphosphonic acid.

Action of bromotriphenylmethane on tricyclohexyl phosphite. A mixture of tricyclohexyl phosphite (2 g) and bromotriphenylmethane (2 g) was heated in a sealed tube at 180° for one hour. The contents of the tube consisted of a thick, slightly colored liquid, at the bottom of which a resin had formed. After an addition of 15% hydrochloric acid (10 ml), the tube was again heated at 190° for two hours. When the tube had cooled, hairlike crystals of triphenylmethylphosphonic acid were precipitated in the aqueous layer. The crystals melted, after purification, at 277-278°.

SUMMARY

1. Reliable methods for the preparation of dicyclohexylphosphorous acid, of dicyclohexyl phosphorochloridite, and of tricyclohexyl phosphite have been found.

2. The following mixed esters of phosphorous acid have been prepared: methyl, ethyl, butyl, and benzyl dicyclohexyl; and cyclohexyl o-phenylene.

3. Methyl, ethyl, butyl, and benzyl dicyclohexyl phosphites react with cuprous halides, forming viscous liquids that do not crystallize.

4. Tricyclohexyl phosphite and cyclohexyl o-phenylene phosphite form well crystallizing complex compounds with cuprous bromide.

5. Methyl, ethyl, butyl, and benzyl dicyclohexyl phosphites behave in a peculiar fashion in the isomerization reaction with the corresponding alkyl halides at 200-220°, cyclohexane and the corresponding alkylphosphonic acids being formed.

Received June 23, 1952

A. E. Arbuzov Chemical Institute
Kazan Institute Affiliated to the
USSR Academy of Sciences

LITERATURE CITED

[1] H. G. Cook, J. D. Hett et al. J. Chem. Soc. 2921 (1949).

[2] A. E. Arbuzov and B. A. Arbuzov, J. Russ. Phys. Chem. Soc. 61, 1923 (1929).

[3] A. E. Arbuzov and F. G. Valitova, Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 4, 533 (1940).

[4] A. E. Arbuzov, "Catalysis Phenomena Associated with the Reactions of certain Phosphorus Compounds", A monograph, p. 144 (1914).

COMPLEX COMPOUNDS OF PHOSPHOROUS ESTERS

COMMUNICATION 1. COMPOUNDS WITH COPPER, SILVER, AND GOLD SALTS

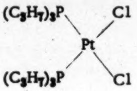
A. E. Arbuzov and V. M. Zoroastrova

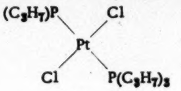
The complex compounds of phosphines and arsines with metal salts have been studied in some detail, and their investigation is being pursued with vigor at the present time. The complex compounds formed with tertiary phosphines comprise the following principal types [1]:

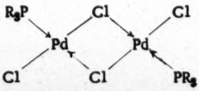
Bromides and iodides of univalent copper and silver unite with phosphines, giving a type of complex (I and II) having a quadruple molecular weight: $[R_3P{\cdot}CuI]_4$ (I), and $[R_3P{\cdot}AgI]_4$ (II).

Halides of univalent gold give simple linear molecules of the type: $R_3P \longrightarrow AuCl$ (III).

Salts of bivalent metals, e.g., palladous chloride or platinous chloride, give complex compounds of the following types: those formed from one molecule of salt, $(R_3P)_2PdCl_2$ (IV), having a planar configuration and being able to exist in cis and trans forms (V and VI), and bridged forms (VII), having a planar molecule of trans configuration:


(V) (cis)


(VI) (trans)


(VII)

The halides of mercury and cadmium give compounds conforming to types IV and VII in constitution, but having a tetrahedral arrangement about the central atom. Mercury and cadmium salts may give also compounds of the types $[(R_3P)_2\,(HgBr_2)_3]$ and $[(R_3P)_2\,(HgBr_2)_4]$.

The complex compounds of phosphorous esters have been studied to a considerably less extent. Schutzenberger [2] by the action of alcohols on $PtCl_2{\cdot}PCl_3$ and $PtCl_2{\cdot}2PCl_3$ obtained $PtCl_2{\cdot}P(OCH_3)_3$, and $PtCl_2{\cdot}2P(OCH_3)_3$, $PtCl_2{\cdot}P(OC_2H_5)_3$ and $PtCl_2{\cdot}2P(OC_2H_5)_3$. Pomey [3] prepared $PtCl_2{\cdot}P(OC_3H_7)_3$, and Risler [4] prepared $PtCl_2{\cdot}P(OC_5H_{11})_3$ by similar methods. Lindet [5] by the action of methanol and of ethanol on $AuCl{\cdot}PCl_3$, obtained $AuCl{\cdot}P(OCH_3)_3$ and $AuCl{\cdot}P(OC_2H_5)_3$.

One of us [6] has shown that full esters of phosphorous acid give complex compounds with cuprous halides of the types $CuX{\cdot}P(OR)_3$ and $CuX{\cdot}2P(OR)_3$. Full esters of phosphorous acid react also with silver halides giving complex compounds of the type $AgX{\cdot}P(OR)_3$ [7].

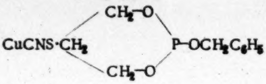
Grinberg and Troitskaya [8] prepared a number of complex platinum compounds, using trialkyl phosphites and dialkylphosphorous acids as addends, and studied their properties. In this work a strong analogy was revealed between phosphonic and phosphorous derivatives. Recently, we have undertaken a more detailed study of the previously prepared complex compounds of full phosphorous esters, and we have prepared new complex derivatives of trialkyl phosphites.

In the present communication we give the results on copper, silver and gold compounds. As already indicated, full phosphorous esters give complexes of the types $CuX{\cdot}P(OR)_3$ and $CuX{\cdot}2P(OR)_3$, with cuprous halides.

Molecular weights have already been determined for some of the compounds of the first type [6]. Ebullioscopic measurements in chloroform on $CuCl \cdot P(OCH_3)_3$ and $CuBr \cdot P(OCH_3)_3$ gave for the first compound M = 374 instead of 223.5, or for the double molecule 447, and for the second compound 576 instead of 268, or for the double molecule 536. Cryoscopic measurements in benzene on $CuI \cdot P(OC_2H_5)_3$ gave M = 1088, corresponding to a triple molecular weight (1071). Thus the results obtained do not give a clear idea of the molecular weights of these complex compounds.

Since partial decomposition of the complex may occur in the course of molecular-weight determination in boiling chloroform, we have measured the molecular weights cryoscopically in benzene and have obtained the results given in Table 1.

TABLE 1

No.	Formula	B.p. °C	Molecular weight	
			found	calculated
1	$[CuCl \cdot P(OC_3H_7)_3\text{-}i]_3$	112-114	921.6	921.57
2	$[CuBr \cdot P(OC_3H_7)_3\text{-}i]_3$	149-150	1059.8	1054.9
3	$[CuI \cdot P(OC_3H_7)_3\text{-}i]_3$	184-185	1192.6	1195.98
4	$[CuCl \cdot P(OC_6H_5)_3]_3$	95- 96	1220.1	1227.5
5	$[CuBr \cdot P(OC_6H_5)_3]_3$	90.5-91.5	1363.8	1360.8
			1342.4	
6	$[CuCNS \cdot P(OC_3H_7)_3\text{-}i]_3$	95-96	1047.8	989.4
7		150-152 (dec.)		

Results are given in Table 1 for the new complex compound of triisopropyl phosphite with copper thiocyanate which we have prepared. The molecular-weight results show that complexes of the type $CuX \cdot P(OR)_3$ have triple molecules and differ, therefore, from the analogous complexes with phosphines ($CuX \cdot PR_3$), to which quadrupled molecular weights are ascribed [9]. It should be noted, however, that the experimental values for the molecular weights of $CuX \cdot PR_3$ lie between the triple and quadruple values.

Molecular weights have hitherto not been determined for compounds of the type $CuX \cdot 2P(OR)_3$. We have determined the molecular weights cryoscopically in benzene and have thus shown that the compounds $CuX \cdot 2P(OR)_3$ are in the form of simple molecules (Table 2).

TABLE 2

No.	Formula	B.p. °C	Molecular weight	
			found	calculated
1	$CuCl \cdot 2P(OC_6H_5)_3$	70	606.3	719.2
2	$CuBr \cdot 2P(OC_6H_5)_3$	73-74	697.4	763.7
3	$CuI \cdot 2P(OC_6H_5)_3$	73-76	713.1	810.7

We have found no data in the literature concerning compounds of the type $CuX \cdot 2PR_3$. Nyholm [10] has recently described the complexes $CuX \cdot 2AsR_3$. Cryoscopic measurements of molecular weight in benzene and nitrobenzene gave figures lying between the single and double values. Nyholm considers the double value to be the more probable, the observed lowering of the value being probably to be explained by dissociation of the complex in solution; but he considers that the question of the molecular weight of $CuX \cdot 2AsR_3$ remains open.

It is interesting to note that cryoscopic measurements in benzene and in nitrobenzene of the molecular weights of the complexes $CuX \cdot AsR_3$ give, according to Nyholm, values that correspond to triple molecules, although Nyholm assumes quadruple values for them.*

A. E. Arbuzov and Kartashev [7] have obtained by the action of triethyl phosphite on silver salts the complexes $(C_2H_5O)_3P \cdot AgX$, where X = Cl, Br and I. These complexes were not investigated more closely.

We have obtained hitherto undescribed complexes of AgX with isopropyl phosphite and have determined their molecular weights cryoscopically in benzene. The results are given in Table 3.

* For $CuCl \cdot AsR_3$ the calculated molecular weight is 343, and the values found are 1205 (nitrobenzene) and 1020 (benzene); the calculated values for trimer and tetramer are 1029 and 1372 respectively. For $CuBr \cdot AsR_3$ the calculated molecular weight is 387.5, and the value found in benzene is 1260; the calculated value for trimer is 1162.5.

TABLE 3

No.	Formula	B.p. °C	Molecular weight	
			found	calculated
1	$[AgCl \cdot P(OC_3H_7)_3\text{-}i]_3$	29-30	814.4 1233.3	1054
2	$[AgBr \cdot P(OC_3H_7)_3\text{-}i]_3$	73-75	1216.5	1187.9
3	$[AgI \cdot P(OC_3H_7)_3\text{-}i]_3$	163-164	1326.9	1328.9

As will be seen from Table 3, the complexes of triisopropyl phosphite with AgX (X = Cl, Br and I) have triple molecules in benzene solution and are therefore analogous to the complexes $CuX \cdot P(OR)_3$. It should be noted that the complexes $CuX \cdot PR_3$ and $AgX \cdot PR_3$ have the same type of structure and have association factors in benzene solution of between 3.5 and 4. We have not succeeded in preparing compounds between triphenyl phosphite and silver halide.

As already stated, Lindet [5] by the action of methanol and of ethanol on the complex $AuCl \cdot PCl_3$ has obtained the complexes $AuCl \cdot P(OCH_3)_3$ and $AuCl \cdot P(OC_2H_5)_3$. We have prepared the complex with trimethyl phosphite by three different methods: a) by Lindet's method, by the action of trimethyl phosphite on $AuCl \cdot PCl_3$, b) by the action of trimethyl phosphite on AuCl, and c) by the action of trimethyl phosphite on $AuCl \cdot PCl_3$. In all cases the same compound of m.p. 101-102° was obtained. Also, we have obtained by the action of triphenyl phosphite on $AuCl \cdot PCl_3$ the previously undescribed complex $(C_6H_5O)_3P \cdot AuCl$, m.p. 103°, and we have prepared a liquid complex of AuCl with triisopropyl phosphite.

Molecular-weight determinations by cryoscopy in benzene of the crystalline complexes obtained gave results corresponding to single molecules (Table 4).

TABLE 4

No.	Formula	B.p. °C	Molecular weight	
			found	calculated
1	$(CH_3O)_3P \cdot AuCl$	101-102	348	356.7
2	$(C_6H_5O)_3P \cdot AuCl$	103	514.4	542.5

Thus, the complexes formed between phosphorous esters and gold (I) chloride have structures analogous to those of the complexes between gold (I) chloride and phosphines.

EXPERIMENTAL

Molecular Weight Determinations by the Cryoscopic Method on Complex Compounds formed between Triisopropyl Phosphite and Cuprous Halides

Compounds 1, 2 and 3 were prepared first by A. E. Arbuzov in 1905.

1) $P(OC_3H_7)_3 \cdot CuCl$, m.p. 112-114° (from petroleum ether)
2) $P(OC_3H_7)_3 \cdot CuBr$, m.p. 149-150° (from petroleum ether)
3) $P(OC_3H_7)_3 \cdot CuI$, m.p. 184-185° (from ether)

Compound 1:

Found: M 921.6
Calculated for $[P(OC_3H_7\text{-}i)_3 \cdot CuCl]$: M 307.19
" $[P(OC_3H_7\text{-}i)_3 \cdot CuCl]_3$: M 921.57

Compound 2:

Found: M 1059.8
Calculated for $[P(OC_3H_7\text{-}i)_3 \cdot CuBr]$: M 351.64
" $[P(OC_3H_7\text{-}i)_3 \cdot CuBr]_3$: M 1054.95

Compound 3:

Found: M 1192.6
Calculated for $[P(OC_3H_7\text{-}i)_3 \cdot CuI]$: M 398.65
" $[P(OC_3H_7\text{-}i)_3 \cdot CuI]_3$: M 1195.95

Determination of the Molecular Weights of Complex Compounds formed between Triphenyl Phosphite and Cuprous Halides

Five compounds formed between triphenyl phosphite and cuprous halides are known (they were first prepared by A. E. Arbuzov):

1) $CuCl \cdot P(OC_6H_5)_3$, m.p. 95-96°
2) $CuBr \cdot P(OC_6H_5)_3$, m.p. 90.5-91.5°
3) $CuCl \cdot 2P(OC_6H_5)_3$, m.p. 70°
4) $CuBr \cdot 2P(OC_6H_5)_3$, m.p. 73-74°
5) $CuI \cdot 2P(OC_6H_5)_3$, m.p. 73-76°

The molecular weights were determined cryoscopically in benzene:

Compound 1:

Found: M 1220.1
Calculated for $[CuCl \cdot P(OC_6H_5)_3]$: M 409.15
" $[CuCl \cdot P(OC_6H_5)_3]_3$: M 1227.45

Compound 2:

Found: M 1363.8; 1342.4
Calculated for $[CuBr \cdot P(OC_6H_5)_3]$: M 453.61
" $[CuBr \cdot P(OC_6H_5)_3]_3$: M 1360.83

Compound 3:

Found: M 606.3
Calculated for $CuCl \cdot 2P(OC_6H_5)_3$: M 719.24

Compound 4:

Found: M 697.4
Calculated for $CuBr \cdot 2P(OC_6H_5)_3$: M 763.72

Compound 5:

Found: M 713.1
Calculated for $CuI \cdot 2P(OC_6H_5)_3$: M 810.7

Preparation of Complex Compounds between Phosphorous Esters and Salts of Silver, Copper, and Gold

1. Preparation of $P(OC_3H_7\text{-}i)_3AgCl$. Silver chloride (0.73 g) was added to triisopropyl phosphite (1.2 g). The temperature of the reaction mixture rose to 40°, but in order to dissolve the residual salt the mixture was cautiously heated over a burner at 50-55°. When reaction was complete, the product was dissolved in absolute alcohol; the small amount of precipitate present was filtered off, and the solution was poured into snow-cooled water. The oil that separated crystallized when rubbed out with a glass rod. The crystals obtained melted at 28-30°. After being recrystallized from ether, the product melted at 29-30°.

Found %: Cl 9.83
$C_9H_{21}O_3PAgCl$. Calculated %: Cl 10.08

Determination of the molecular weight cryoscopically in benzene gave the following result:

Found: M 814.4
Calculated for $[P(OC_3H_7\text{-}i)_3 \cdot AgCl]$: M 351.5
" $[P(OC_3H_7\text{-}i)_3 \cdot AgCl]_3$: M 1054

2. Preparation of $P(OC_3H_7\text{-}i)_3 \cdot AgBr$. Silver bromide (1.7 g) was added in portions to triisopropyl phosphite (1.8 g, i.e., one mole per mole of the salt). As in the first experiment, the mixture became warm with the reaction. When the temperature fell, the mixture was heated to 50° and dissolved in absolute alcohol; it was then filtered and poured into cold water. The oil that formed solidified rapidly. The crystalline product was filtered off, dried on filter paper, and recrystallized from dry ether, giving colorless crystals (2.3 g), m.p. 73-75°, soluble in many organic solvents, but insoluble in water; in presence of water and in the light they darkened with separation of silver.

Found %: Br 20.39
$C_9H_{21}O_3PAgBr$. Calculated %: Br 20.18

Found: M 1233.3; 1216.5 (cryoscopic)
Calculated for $[P(OC_3H_7\text{-}i)_3 \cdot AgBr]$: M 395.95
" $[P(OC_3H_7\text{-}i)_3 \cdot AgBr]_3$: M 1187.85

3. Preparation of $P(OC_3H_7\text{-}i)_3 \cdot AgI$. The complex compound of triisopropyl phosphite with silver iodide was obtained by a method similar to that just described from 1 g of the ester and 1.17 g of the salt. To complete the reaction, the mixture was carefully heated at 50-55° over a bunsen flame. When the test tube was cooled, the product rapidly solidified. Two crystallizations from ether and one from absolute alcohol yielded well formed colorless crystals of m.p. 163-164° (dec). The reaction product was similar to the previous products in properties: soluble in ether, benzene, acetone, methanol, and ethanol; insoluble in water; yellows on standing.

Found %: I 28.83
$C_9H_{21}O_3PAgI$. Calculated %: I 28.65

Found: M 1326.9 (cryoscopic)
Calculated for $[P(OC_3H_7\text{-}i)_3 \cdot AgI]$: M 442.97
" $[P(OC_3H_7\text{-}i)_3 \cdot AgI]_3$: M 1328.91

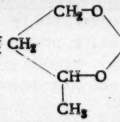
4. Action of silver halides on triphenyl phosphite. Silver iodide (1.2 g) was added to triphenyl phosphite (1.5 g). Reaction did not set in: the temperature remained unchanged, and the salt did not dissolve in the ester. The mixture was heated, at first at 55°, later at a higher temperature (about 100°), and finally at 150-155°. Part of the silver iodide then dissolved. After treatment of the reaction mixture with absolute alcohol and with water, an oil was obtained which did not crystallize after strong cooling and long standing. Attempts to prepare complex compounds of triphenyl phosphite with silver bromide and with silver chloride also did not give positive results.

5. Preparation of the complex compound of triisopropyl phosphite with cuprous thiocyanate. Cuprous thiocyanate (1.4 g) was added to triisopropyl phosphite (2.2 g). Reaction set in, and the temperature of the mixture rose to 60°. The white greasy material that formed solidified on standing. After several recrystallizations from absolute ether, a product was obtained that melted with decomposition at 95-96°. It was of good solubility in ether, benzene, acetone, ligroin, methanol, and ethanol. From its solutions, a precipitate of cuprous thiocyanate separated on standing.

Found %: P 9.64; 9.81; S 9.88
$C_{10}H_{21}O_3PCuNS$. Calculated %: P 9.40 S 9.72

Found: M 1047.8 (cryoscopic)
Calculated for $[P(OC_3H_7\text{-}i)_3 \cdot CuCNS]$: M 329.8
" $[P(OC_3H_7\text{-}i)_3 \cdot CuCNS]_2$: M 659.5
" $[P(OC_3H_7\text{-}i)_3 \cdot CuCNS]_3$: M 989.4

6. Preparation of the complex compound of triphenyl phosphite with cuprous thiocyanate. Cuprous thiocyanate (0.8 g) was added to triphenyl phosphite (2 g, i.e., one mole per mole of the thiocyanate). A very slow reaction with insignificant rise in temperature set in (in 7-10 minutes the temperature rose from 20° to 26°). The mixture was heated at 85-90° on the water bath for several minutes. On cooling, a solid gray mass was formed which was readily soluble in ether, benzene, and other solvents, but insoluble in water. When practically the whole of the solvent had been evaporated off, there remained a white solid having a wide melting range (50-56°). The product melted to a milky liquid, which did not resolidify on cooling. It was not found possible to obtain a product having a sharp melting point.

7. Preparation of 

$POCH_2C_6H_5 \cdot CuCNS$. Cuprous thiocyanate (0.46 g) was added to benzyl 1-methyltrimethylene phosphite (0.8 g, i.e., one mole per mole of CuCNS). The temperature of the mixture rose to 50°, and a thick white mass was formed. To complete the reaction, the mixture was heated for ten minutes in a glycerol bath at 80°. It was then treated with benzene. After evaporation of the benzene, a solid remained in the dish; it was soluble in ether, alcohol, acetone, and dioxane, but was insoluble in water. It melted at 150-152° (it began to sinter together somewhat below this temperature). Its alcoholic solution rapidly became turbid owing to separation of CuCNS.

Found %: P 8.40; S 10.28
$C_{11}H_{15}O_3PCuCNS$. Calculated %: P 8.91; S 9.21

8. Preparation of the complex compound of trimethyl phosphite with aurous chloride. Expt. 1. Action of methanol on the complex AuCl·PCl$_3$. The inorganic complex of aurous chloride with phosphorus trichloride was prepared by heating aurous chloride with excess of phosphorus trichloride for two hours under reflux (Schutzenberger's method). In the flask, after removal of excess of phosphorus trichloride, there remained long needles of the complex, which are extremely unstable to atmospheric moisture. A small amount of the AuCl·PCl$_3$ complex was dissolved in excess of absolute methanol. Reaction proceeded with inappreciable evolution of heat. On evaporation of the methanol, grayish crystals came down, and these, after recrystallization from methanol, were obtained as colorless needles, m.p. 101-102°. When heated above the melting point, the product darkened and metallic gold separated out.

Expt. 2. Action of trimethyl phosphite on the complex AuCl·PCl$_3$. Trimethyl phosphite (0.17 g) was added to AuCl·PCl$_3$ (0.5 g, i.e., one mole per mole of phosphite) and was dissolved in dry benzene (4 ml). The excess of benzene and phosphorus trichloride was removed under reduced pressure. On standing, crystals came down which, after being washed with ether, melted at 95-101°. The product was purified by recrystallization from methanol, giving needles, m.p. 101°, which melted, in admixture with the product obtained in Expt. 1, at 101-102°.

Expt. 3. Action of AuCl on trimethyl phosphite. Trimethyl phosphite (0.28 g) was dissolved in dry ether (5 ml). An equimolecular proportion of aurous chloride was added to the solution in small amounts at a time, and the substances reacted with evolution of much heat and with separation of a small amount of colloidal gold. After evaporation of the ether, crystals of m.p. 101° were obtained in insignificant yield. It was undepressed in melting point when mixed with the product of Expt. 1. It was of good solubility in ether, benzene, and alcohol, but insoluble in water. The molecular weight was determined cryoscopically in benzene:

Found: M 348
$C_3H_9O_3PAuCl$. Calculated: M 356.73

9. Preparation of the complex compound of triisopropyl phosphite with aurous chloride. Expt. 1. Action of isopropyl alcohol on the complex AuCl·PCl$_3$. A small amount of the complex AuCl·PCl$_3$ was treated with anhydrous isopropyl alcohol. The mixture grew warm. When the excess of isopropyl alcohol had been removed under reduced pressure, a liquid product, which could not be caused to crystallize, remained in the flask.

Expt. 2. Action of AuCl on triisopropyl phosphite. a) Aurous chloride (0.16 g) was added in two portions to triisopropyl phosphite (0.28 g, i.e. one mole per mole of AuCl). With each addition of the salt, the temperature of the mixture rose to 43-45°. The reaction product was treated with dry ether, and the solution was filtered from the small residue of AuCl and was set aside for crystallization. However, when the ether had evaporated, the product did not crystallize. Snow cooling did not induce crystallization.

b) The experiment was carried out in ether solution, triisopropyl phosphite (0.34 g) dissolved in dry ether being treated with an equimolecular proportion of aurous chloride. Reaction occurred with evolution of heat and hissing (boiling of the ether at the point at which the reagents came into contact). The liquid first became yellow, and then became colorless again. It was filtered, and the clear liquid was left in a desiccator over sulfuric acid. After the liquid had stood overnight, the walls of the flask were covered with a gold mirror.

10. Preparation of the complex compound of triphenyl phosphite with aurous chloride. Triphenyl phosphite was added dropwise to AuCl·PCl$_3$ (1.2 g) in benzene solution. Reaction occurred, and the mixture grew warm. When a part of the benzene had been evaporated, large glistening crystals (0.8 g, prisms) came down. The product, after recrystallization from ether, melted at 103° (when it was heated further, metallic gold separated). It was soluble in ether, benzene, acetone, and other solvents, but insoluble in water. After being stored for a long time, it became dirty pink in color.

Found %: Au 35.81; P 5.74
$C_{18}H_{15}O_3PAuCl$. Calculated %: Au 36.33; P 5.71

Found: M 514.43 (cryoscopic)
$C_{18}H_{15}O_3PAuCl$. Calculated: M 542.48

SUMMARY

1. The synthesis has been performed for the first time of complex compounds of triisopropyl phosphite with silver halides and of complex compounds of triisopropyl phosphite and of benzyl 1-methyltrimethylene phosphite with cuprous thiocyanate.

2. The molecular weights have been determined by the cryoscopic method of complex compounds of certain full esters of phosphorous acid with copper and silver halides. For compounds of the type $P(OR)_3 \cdot AgX$, $P(OR)_3 \cdot CuX$, $P(OR)_3 \cdot CuCNS$, values corresponding to triple molecules have been obtained.

3. Complex compounds of triisopropyl phosphite and of triphenyl phosphite with aurous chloride have been synthesized. Determination of their molecular weights by the cryoscopic method (benzene solution) has shown that they occur in the monomeric form.

Received June 23, 1952

A. M. Butlerov Chemical Research Institute
of the V. I. Ulyanov-Lenin Kazan State University

LITERATURE CITED

[1] J. Allison and F. Mann, J. Chem. Soc. 2915 (1949).

[2] P. Schutzenberger, Bull. Soc. chim. 17, 482 (1872); 18, 101 (1872).

[3] E. M. Pomey, Jahresber. 612 (1887).

[4] M. Risler, Bull. Soc. chim. 18, 151 (1872).

[5] M. L. Lindet, Ann. Chim. (6) 11, 190 (1887).

[6] A. E. Arbuzov, "The Structure of Phosphorous Acid and its Derivatives", St. Petersburg, 1905, p. 32.

[7] A. E. Arbuzov and A. V. Kartashev, J. Russ. Phys. Chem. Soc. 45, 79 (1913).

[8] A. A. Grinberg and A. D. Troitskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 4, 178 (1944); A. A. Grinberg, Z. A. Razumova, and A. D. Troitskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 3, 253 (1946).

[9] F. Mann, D. Purdie and A. Wells, J. Chem. Soc. 1506 (1936).

[10] R. S. Nyholm, J. Chem. Soc. 1257 (1952).

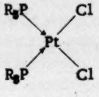
BLANK
PAGE

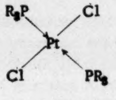
COMPLEX COMPOUNDS OF PHOSPHOROUS ESTERS

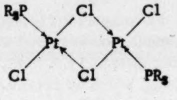
COMMUNICATION 2. COMPLEX COMPOUNDS WITH PLATINOUS SALTS

A. E. Arbuzov and V. M. Zoroastrova

Two types of complex compound formed between tertiary phosphines and platinous salts have been prepared: simple complexes, which occur in cis and trans forms (I and II), and bridged forms, which can theoretically exist in three isomeric forms, but have been isolated up till the present time only in the trans form (III) [1,2]:

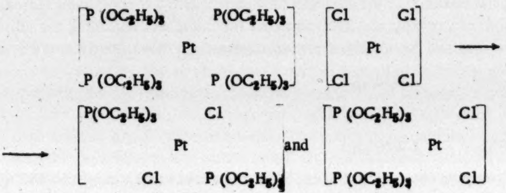

(I) (cis)


(II) (trans)


(III)

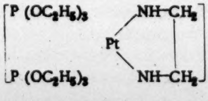
The study of the complex compounds of bivalent platinum was initiated by the work of Schutzenberger [3], Pomey [4], and Risler [5]. The physical properties of the complexes obtained remained practically without description by these authors. Rosenheim [6] attempted to isolate the isomeric compounds $PtCl_2 \cdot 2P(OC_2H_5)_3$, but succeeded in isolating only one compound, to which he arbitrarily ascribed the trans configuration. For the compound $PtCl_2 \cdot P(OC_2H_5)_3 \cdot C_6H_5NH_2$ he isolated two isomers, m.p. 147° and 108°. To the high-melting form he ascribed the trans structure, and to the low-melting form the cis structure. Rosenheim established that the compounds $PtCl_2 \cdot PCl_3$ and $PtCl_2 \cdot P(OR)_3$ have double molecules.

Considerably later, complex compounds of bivalent platinum were studied by Grinberg and Troitskaya [7]. Unlike previous investigators, Grinberg and Troitskaya prepared phosphite complexes not by the action of alcohols on $PtCl_2 \cdot PCl_3$ or $PtCl_2 \cdot 2PCl_3$, but by the reaction of triethyl phosphite with potassium chloroplatinate (II) in aqueous solution. In this way these authors prepared the compound $[Pt\{P(OC_2H_5)_3\}_4][PtCl_4]$ and a small amount of the substance $[Pt\cdot\{P(OC_2H_5)_2OH\}_2\{P(OC_2H_5)_2O\}_2]$. The first compound, when heated in chloroform, decomposed with formation of two isomers, m.p. 58-59° and 52 - 52.5°.


(trans)

(cis)

On the basis of a study of the reaction of trans isomers with ethylenediamine and with ammonia, a reaction that leads in the case of the isomer of m.p. 58-59° to the products


$PtCl_4$ and $[Pt\{P(OC_2H_5)_3\}_2(NH_3)_2]Cl_2$,

Grinberg and Troitskaya assigned it the cis configuration. By the action of thiourea on the isomer of m.p. 58-59°, instead of observing the expected entry of four molecules of thiourea, they obtained a compound to which they ascribed the following structure:

$[Pt\{P(OC_2H_5)_2OH\}_2\{CS(NH_2)_2\}_2]Cl_2$.

By means of an exchange reaction between the complex $[Pt\{P(OC_2H_5)_3\}_2Cl_2]$ and potassium iodide, Grinberg and Troitskaya obtained the corresponding iodide $[Pt\{P(OC_2H_5)_3\}_2I_2]$, m.p. 85-86°. The same iodide was obtained by them by the action of potassium iodoplatinate (II) on triethyl phosphite. The authors assigned the cis configuration to the compound of m.p. 85-86°. By carrying out the last reaction in the cold, they isolated an unstable form of m.p. 39-49°, to which they assigned the trans structure.

In the present communication results are given of work on the preparation of complexes of phosphorous esters with bivalent platinum by the direct action of platinous chloride on the esters and of work on some of the reactions of these compounds. We have repeated Schutzenberger's experiments and have obtained by his method the complexes $PtCl_2 \cdot PCl_3$ (m.p. 170-173°) and $PtCl_2 \cdot 2PCl_3$ (m.p. ~160°). By the action of methanol and of ethanol on these we have obtained Schutzenberger's complexes $PtCl_2 \cdot 2P(OCH_3)_3$ and $PtCl_2 \cdot 2P(OC_2H_5)_3$, and have determined their melting points (see table). By the direct action of platinous chloride on trimethyl phosphite and on triethyl phosphite, the complexes $PtCl_2 \cdot 2P(OR)_3$ (where R = CH_3 and C_2H_5), identical with the corresponding compounds of Schutzenberger, have been prepared.

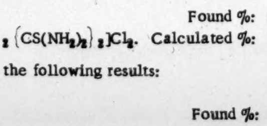
The melting points of the complex $PtCl_2 \cdot 2P(OC_2H_5)_3$, which we obtained from $PtCl_2 \cdot 2PCl_3$, and by the action of $PtCl_2$ on triethyl phosphite, was identical with that of the compound $[Pt\{P(OC_2H_5)_3\}_2Cl_2]$, obtained by Grinberg and Troitskaya from $K_2[PtCl_4]$ and $P(OC_2H_5)_3$. In the table the constants are given of other compounds of the type $PtCl_2 \cdot 2P(OR)_3]$, which we obtained by the direct action of $PtCl_2$ on phosphorous esters. The complexes No. 7 and No. 8, from triisopropyl phosphite and triphenyl phosphite respectively, have not been previously described in the literature.

The molecular weight of the isopropyl ester complex determined cryoscopically and that of the phenyl ester determined by Rast's method in camphor corresponded to monomeric forms.

$PtCl_2 \cdot 2P(OC_3H_7\text{-}i)_3$. Found M 644; calculated M 682.4
$PtCl_2 \cdot 2P(OC_6H_5)_3$. Found M 868.1; calculated M 886.3

Both products consisted of colorless crystals, soluble in many organic solvents and stable to storage.

When $PtCl_2 \cdot 2P(OC_2H_5)_3$ and $PtCl_2 \cdot 2P(OC_3H_7\text{-}i)_3$ react with potassium iodide in aqueous alcohol, an exchange reaction occurs with formation of the corresponding iodides $[PtI_2 \cdot 2P(OC_2H_5)_3]$, m.p. 85-86°, and $[PtI_2 \cdot 2P(OC_3H_7\text{-}i)_3]$, m.p. 137°. The complex $[PtI_2 \cdot 2P(OC_2H_5)_3]$ was found to be identical with Grinberg and Troitskaya's complex obtained from K_2PtI_4 and $P(OC_2H_5)_3$ (mixed m.p. 85°). Somewhat unexpected results were obtained by the action on $PtCl_2 \cdot 2P(OR)_3$ (R = CH_3, C_2H_5 and C_3H_7-i) of thiourea under the conditions indicated by Grinberg and Troitskaya. When we investigated the products of the reaction of thiourea with the complexes indicated, we obtained results that differed from those of Grinberg and Troitskaya for the complex containing the ethyl radical. The analytical results (Pt and P) that we obtained for the three products correspond most closely to the formula:



$$\left[\begin{array}{ccc} (RO)_2POH & & CS(NH_2)_2 \\ & \cdot Pt & \\ CS(NH_2)_2 & & CS(NH_2)_2 \end{array}\right] Cl_2,$$

where R = CH_3, C_2H_5, C_3H_7-i. The products obtained are crystalline substances having m.p. 150-153° (R=CH_3); m.p. 185° (R=C_2H_5) and m.p. 185-187° (R=C_3H_7-i), with decomposition in each case.

For the ethyl compound Grinberg and Troitskaya give the decomposition temperature as 184° and give the following analytical figures:

Found %: Pt 28.31; 28.68; S 9.42
$[Pt\{P(OC_2H_5)_2OH\}_2\{CS(NH_2)_2\}_2]Cl_2$. Calculated %: Pt 28.10; S 9.23

We have obtained the following results:

Found %: Pt 30.78; 30.98; P 4.44; 4.52
S 14.68; 14.59
$[Pt\{P(OC_2H_5)_2OH\}\{CS(NH_2)_2\}_3]Cl_2$. Calculated %: Pt 30.87; P 4.90; S 15.21

For the methyl and isopropyl compounds the analytical figures again correspond to the presence in the compounds of three molecules of thiourea. This replacement of three components of the inner zone by thiourea molecules is unusual [8], and the interesting question of the nature of the products of the action of thiourea on the complexes $[PtCl_2 \cdot 2P(OR)_3]$ requires further study.

TABLE

No.	Formula	M.p. (°C)		
		Our results	Schutzenberger's results	Grinberg and Troitskaya's results
1	$PtCl_2 \cdot PCl_3$ (yellow crystals)	170-173 (dec.)	170	–
2	$PtCl_2 \cdot 2PCl_3$ (colorless crystals)	~160	~160	–
3	$PtCl_2 \cdot P(OCH_3)_3$ (orange crystals)	131-132	–	–
4	$PtCl_2 \cdot 2P(OCH_3)_3$ (colorless crystals)	137-138	–	–
5	$PtCl_2 \cdot P(OC_2H_5)_3$ (orange-yellow)	83	80-83	–
6	$PtCl_2 \cdot 2P(OC_2H_5)_3$ (colorless crystals)	59-60	–	59-60
7	$PtCl_2 \cdot 2P(OC_3H_7\text{-}i)_3$ (colorless crystals)	132-133	–	–
8	$PtCl_2 \cdot 2P(OC_6H_5)_3$ (colorless crystals)	190-191 (dec.)	–	–

EXPERIMENTAL

1. Preparation of the Complex Compound of Platinous Chloride with Phosphorus Trichloride. A mixture of platinum black (3.6 g) and phosphorus pentachloride (3.85 g) was sealed in a glass tube and heated in a sand bath at 230° for two hours. The reaction product was extracted with dry benzene. When the greater part of the solvent had been evaporated off in a stream of dry carbon dioxide, orange needles of the complex $PtCl_2 \cdot PCl_3$ (I), m.p. 170-173° (dec.) came down. It is a very hygroscopic substance, strongly fuming in air. The product was analyzed by heating with sodium carbonate.

Found %: P 7.82; Cl 43.74
$PtCl_2 \cdot PCl_3$. Calculated %: P 7.68; Cl 43.93

2. Preparation of the Complex Compound $PtCl_2 \cdot 2PCl_3$. The compound $PtCl_2 \cdot 2PCl_3$ (II) was obtained from the preceding compound by the action of excess of phosphorus trichloride. When reaction was complete, the phosphorus trichloride was removed under reduced pressure in a stream of dry carbon dioxide. The crystalline grayish-yellow residue was recrystallized from a small amount of benzene; it melted at about 160°. This compound, like the first, is unstable in air.

3. Preparation of $PtCl_2 \cdot P(OCH_3)_3$. Anhydrous methanol (4 ml) was added to the product I (1.92 g). Reaction was accompanied by rise of temperature and evolution of hydrogen chloride. The excess of methanol and hydrogen chloride was removed under reduced pressure in an atmosphere of carbon dioxide. The residue was crystallized from dry benzene, and orange-yellow crystals (1.21 g), which melted at 131-132° with decomposition to a dark-colored liquid, were obtained. The product was soluble in ether, benzene, methanol, and ethanol, but insoluble in water; it was stable in air. It was analyzed as follows: A weighed amount of the substance was heated with concentrated nitric acid (30 drops) in a sealed tube at 200-250° for 5.5 hrs. Oxidation was then complete, and the contents of the tube were poured into a porcelain dish and evaporated on the water bath to dryness. In order to remove nitric acid completely, several additions of concentrated hydrochloric acid were made to the residue. The residue was dissolved in water (100 ml), and concentrated sulfuric and hydrochloric acids (0.3 ml of each) were added. Hydrogen sulfide was passed through the hot solution, and the black precipitate of PtS_2 was filtered off and roasted in a weighed porcelain crucible to give pure platinum. Phosphorus was determined in the filtrate from the separation of platinic sulfide: the clear colorless solution was diluted to 400 ml with water and concentrated sulfuric and nitric acids (10 ml of each) and a 50% solution of NH_4NO_3 were added. The solution was heated on a boiling water bath, and phosphorus was precipitated with ammonium molybdate.

Found %: Pt 51.07; P 8.31
$C_3H_9O_3PCl_2Pt$. Calculated %: Pt 50.03; P 7.94

4. Preparation of $PtCl_2 \cdot 2P(OCH_3)_3$. The preparation of this compound was similar to that of the previous one. The inorganic complex II (1.44 g) was treated with dry methanol. After removal of excess methanol under reduced pressure, crystals appeared. They were contaminated with a grayish incrustation and were purified by recrystallization from methanol, giving colorless crystals (0.9 g) of m.p. 137-138°. Analysis was carried out by oxidation of the substance with concentrated nitric acid in a sealed tube, the platinum being precipitated with hydrogen sulfide, and phosphorus with ammonium molybdate.

Found %: Pt 38.31; P 12.43
$C_6H_{18}O_6P_2Cl_2Pt$: Calculated %: Pt 37.96; P 12.05

The substance $PtCl_2 \cdot 2P(OCH_3)_3$ was prepared also by the action of platinous chloride on trimethyl phosphite. Platinous chloride (1.33 g) was added in small portions to a solution of trimethyl phosphite (0.62 g) in dry benzene (4 ml) (equimolecular proportions of reactants). The temperature of the mixture rose to 42-43°. The products obtained were 0.25 g of crystals, m.p. 137° (from methanol) and a substance (colorless crystals) not containing halogen, m.p. 171-172°. The structure of the latter was not established (analytical figures: Pt 32.67; P 16.90).

5. Preparation of $PtCl_2 \cdot P(OC_2H_5)_3$. This substance was prepared similarly to the trimethyl phosphite compound by the action of dry ethanol on the inorganic complex I. Unlike the methyl compound, the compound of triethyl phosphite with platinous chloride was not readily crystallized out. It forms orange-yellow crystals, m.p. 83°, which can be kept at ordinary temperature for a long time without noticeable change. On being heated to 180°, it decomposes and is converted into a dark-brown liquid.

6. Preparation of $PtCl_2 \cdot 2P(OC_2H_5)_3$. The inorganic complex II was treated with anhydrous ethanol. Hydrogen chloride and the greater part of the alcohol were removed under reduced pressure. A viscous liquid product was obtained which, after standing for several days in a desiccator over sulfuric acid, crystallized out when rubbed out with a glass rod. The product was recrystallized from aqueous alcohol to give colorless crystals, m.p. 59-60° (the recrystallization is conveniently done as follows: the product is dissolved in as little alcohol as possible, about one-third of this volume of water is added, and the mixture is cooled in snow). The compound of m.p. 59° was obtained also by the direct action of $PtCl_2$ on $P(OC_2H_5)_3$.

7. Preparation of $PtCl_2 \cdot 2P(OC_3H_7\text{-}i)_3$. The complex compound of triisopropyl phosphite with platinous chloride was prepared by the direct action of the platinum salt on the phosphorous ester.

Expt. 1. Platinous chloride (0.6 g) was added in portions to triisopropyl phosphite (0.47 g, i.e., one mole per mole of $PtCl_2$). Dissolution of the salt was accompanied by rise in the temperature of the mixture to 50°. The reaction product was dissolved in absolute methanol (5 ml) and separated from the unchanged $PtCl_2$ (0.23 g). Faintly colored crystals (dirty pink) came down on standing. After a second crystallization from methanol containing animal charcoal, a colorless substance, m.p. 132-133° was obtained; it was soluble in benzene, ether, methanol, and ethanol, but was difficultly soluble in water. Analysis for Pt (oxidation with concentrated nitric acid and precipitation with hydrogen sulfide) gave a result corresponding to the formula $PtCl_2 \cdot 2P(OC_3H_7\text{-}i)_3$.

Found %: Pt 28.56; P 9.25
$C_{18}H_{42}O_6P_2PtCl_2$. Calculated %: Pt 28.60; P 9.08

Expt. 2. Platinous chloride (0.67 g) was added in small portions to triisopropyl phosphite (1.04 g, i.e. two moles per mole of platinum salt) diluted with a small amount of dry benzene. The addition of each portion was accompanied by evolution of heat with rise in temperature to 50° or somewhat higher. A crystalline product m.p. 132-133° was obtained from methanol. Its molecular weight in benzene solution was determined cryoscopically.

Found: M 644; $C_{18}H_{42}O_6P_2PtCl_2$. Calculated: M 682.47.

8. Preparation of $PtCl_2 \cdot 2P(OC_6H_5)_3$. Platinous chloride (0.24 g) was added to a solution of freshly distilled triphenyl phosphite (0.6 g, i.e. two moles per mole of platinum salt) in dry benzene (2 ml). The mixture was heated cautiously until the salt was almost completely dissolved. When the benzene solution was cooled, fine glistening crystals, m.p. 186-189° (dec.) came down. Recrystallization from benzene yielded well formed, colorless prisms, (0.28 g) m.p. 190-191° (dec.). The product was readily soluble in acetone, hot alcohol, hot benzene, and dioxane; it was poorly soluble in ether and insoluble in water.

Found %: Pt 21.74
$C_{18}H_{30}O_6P_2PtCl_2$. Calculated %: Pt 22.02

It was found in a separate experiment that a product of the same composition is formed by mixing equimolecular proportions of $PtCl_2$ and triphenyl phosphite. The molecular weight of the product was determined by Rast's method.

Found: M 868.1
$C_{36}H_{30}O_6P_2PtCl_2$ Calculated: M 886.39

Attempts to determine the molecular weight cryoscopically in benzene or dioxane were not successful owing to the sharp reduction in the solubility of the product on cooling (during the determination, the substance crystallized out from the solution).

9. Reaction of $PtCl_2 \cdot 2P(OCH_3)_3$ with potassium iodide. A solution of potassium iodide (0.17 g) in water (1 ml) was added dropwise to a warm solution prepared by heating the compound $PtCl_2 \cdot 2P(OCH_3)_3$ (0.5 g) with methanol (4 ml). The addition of each drop was accompanied by separation of some yellow precipitate. The product obtained (0.6 g) melted, after crystallization from alcohol, at 145-147° (dec.); it consisted of light-yellow crystals, soluble in hot alcohol, in acetone, and in benzene, not very soluble in ether, and insoluble in water.

Found %: Pt 27.88; P 8.90
$C_6H_{18}O_6PtI_2$. Calculated %: Pt 28.00; P 8.89

10. Reaction of $PtCl_2 \cdot 2P(OC_2H_5)_3$ with potassium iodide. The compound of m.p. 59-60° (0.3 g) was dissolved in ethanol (3 ml). To this alcoholic solution, an aqueous solution of potassium iodide (0.26 g) was added, and a yellow precipitate formed immediately. It was filtered off and recrystallized from alcohol (this compound, like the complex compound of trimethyl phosphite with PtI_2, is much more soluble in hot alcohol than in cold). The substance obtained (0.3 g) melted at 85-86° to a yellow liquid. When mixed with Troitskaya's product [9] it melted at 85°. It was of good solubility in benzene, acetone, and ether, but was insoluble in water.

Found %: Pt 24.58; P 7.84
$C_{12}H_{30}O_6P_2PtI_2$, Calculated %: Pt 24.96; P 7.93

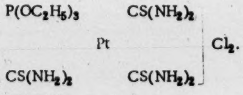
11. Reaction of $PtCl_2 \cdot 2P(OC_3H_7\text{-}i)_3$ with potassium iodide. To a solution of $PtCl_2 \cdot 2P(OC_3H_7\text{-}i)_3$ (0.1 g) in absolute methanol (3 ml), a solution of potassium iodide (0.09 g) in water (7 ml) was added drop by drop. With the addition of the first few drops the solution turned yellow, and further additions led to the appearance of yellow crystals. When the whole of the potassium iodide solution had been added, the yellow product was filtered off and recrystallized from methanol. The substance obtained (0.1 g) melted at 137° and was similar in properties to the analogous triethyl phosphite compound.

Found %: Pt 22.80; P 7.07
$C_{18}H_{42}O_6P_2PtI_2$. Calculated %: Pt 22.56; P 7.00

12. Reaction of $PtCl_2 \cdot 2P(OCH_3)_3$ with thiourea. A mixture of the complex (0.55 g) and thiourea (0.65 g) was dissolved in water (3 ml). Concentrated hydrochloric acid was added, and a colorless crystalline precipitate rapidly made its apperance. It was filtered off (0.11 g) and found to have an indefinite melting point: 105-120° with decomposition. After some time, a second crop of crystals was obtained. This product was yellowish in color and, after crystallization from hydrochloric acid, it melted with decomposition at 150-153°, forming a yellow liquid. A yield of 0.15 g* was obtained.

Found %: Pt 32.46; P 4.79
$C_5H_{19}O_3PPtCl_2S_3N_6$. Calculated %: Pt 32.29; P 5.12

13. Reaction of $PtCl_2 \cdot 2P(OC_2H_5)_3$ with thiourea. Concentrated hydrochloric acid was added to a solution of $PtCl_2 \cdot 2P(OC_2H_5)_3$ (0.9 g) and thiourea (2.7 g) in water (10 ml). After 15-20 minutes, colorless needlelike crystals began to precipitate from the solution. They were filtered off (0.6 g). The substance was twice reprecipitated with ether from its solution in methanol. It melted at about 185° with considerable decomposition; on melting, it became bright yellow in color. The substance was not soluble in ether, benzene, or acetone; it was of low solubility in water, but dissolved in methanol.

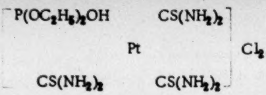


$$\left[\begin{matrix} P(OC_2H_5)_3 & & CS(NH_2)_2 \\ & Pt & \\ CS(NH_2)_2 & & CS(NH_2)_2 \end{matrix}\right]Cl_2.$$

Found %: Pt 30.78; 30.98; P 4.44; 4.52; S 14.68; 14.59
Calculated %: Pt 29.55; P 4.69; S 14.54

---

* The low yield of the product arises from its high solubility in water.



$$\left[\begin{array}{ccc} P(OC_2H_5)_2OH & & CS(NH_2)_2 \\ & Pt & \\ CS(NH_2)_2 & & CS(NH_2)_2 \end{array}\right]Cl_2.$$

Calculated %: Pt 30.87; P 4.90; S 15.26

14. Reaction of $PtCl_2 \cdot 2P(OC_3H_7\text{-}i)_3$ with thiourea. The product of m.p. 132-133° (0.17 g) and thiourea (0.3 g) were dissolved in water (5 ml). To the colorless solution obtained, ten drops of concentrated hydrochloric acid were added. The solution was shaken, and a white crystalline precipitate (0.14 g) soon began to make its appearance. The product was similar in outward appearance and other properties (solubility, effect of heat) to the corresponding ethyl compound. On being heated to 185-187°, it melted with much frothing to a yellow liquid.

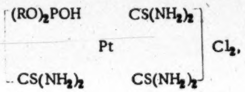
	Found %:	Pt 28.42; 28.23;	P 4.49; 4.83
$C_{12}H_{33}O_3PPtS_3N_6Cl_2$.	Calculated %:	Pt 27.78;	P 4.41
$C_9H_{27}O_3PPtS_3N_6Cl_2$.	Calculated %:	Pt 29.55;	P 4.69

SUMMARY

1. Compounds of the general formula $PtCl_2 \cdot 2P(OR)_3$, where R = CH_3, C_2H_5, C_3H_7-i, and C_6H_5, have been prepared by the action of platinous chloride on trialkyl phosphites, and some of their properties have been studied. The methyl and ethyl compounds were found to be identical with the complexes obtained by the action of methanol and ethanol respectively on $PtCl_2 \cdot 2PCl_3$.

2. By means of an exchange reaction with potassium iodide, $PtCl_2 \cdot 2P(OC_2H_5)_3$ and $PtCl_2 \cdot 2P(OC_3H_7\text{-}i)_3$ have been converted into the corresponding iodides.

3. By the action of thiourea on the complexes $PtCl_2 \cdot 2P(OR)_3$ (where R = CH_3; C_2H_5; C_3H_7-i), crystalline compounds have been prepared which correspond in their analyses to:



$$\left[\begin{array}{ccc} (RO)_2POH & & CS(NH_2)_2 \\ & Pt & \\ CS(NH_2)_2 & & CS(NH_2)_2 \end{array}\right]Cl_2,$$

where R = CH_3; C_2H_5 and C_3H_7-i.

Received June 23, 1952

A. M. Butlerov Chemical Research
Institute of the V. I. Ulyanov-Lenin
Kazan State University

LITERATURE CITED

[1] A. E. Arbuzov and V. M. Zoroastrova, Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 5, 809 (1952).*

[2] K. A. Jensen, Z. anorg. Chem. 229, 250 (1936); J. Chatt, J. Chem. Soc. 2301 (1950); ibid. 652 (1952).

[3] P. Schutzenberger, Bull. Soc. chim. 17, 482 (1872); 18, 101, 144 (1872).

[4] E. M. Pomey, Bull. Soc. chim. 35, 420 (1881).

[5] M. Risler, Bull. Soc. chim. 18, 151 (1872).

[6] A. Rosenheim and W. Loewenstamm, Z. anorg. Chem. 37, 394 (1903); A. Rosenheim and W. Lewy, Z. anorg. Chem. 43, 41 (1905).

[7] A. A. Grinberg and A. D. Troitskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 4, 178 (1944).

[8] N. S. Kurnakov, J. Russ. Phys. Chem. Soc. 25, 565 (1893); A. A. Grinberg and Z. A. Razumova, J. Gen. Chem. 18, 282 (1948).

[9] A. D. Troitskaya, Dissertation, Kazan, 1944.

---

* See Consultants Bureau translation, p. 729.

COMPLEX COMPOUNDS OF PHOSPHOROUS ESTERS

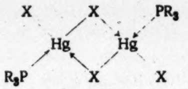
COMMUNICATION 3. COMPLEX COMPOUNDS WITH MERCURY SALTS

A. E. Arbuzov and V. M. Zoroastrova

Tertiary phosphines form a series of complex compounds with the halides of bivalent mercury [1]. The following types of complex have been described [2]:

A) $[(R_3P)_2 \cdot HgX_2]$. This type is given by triarylphosphines, but not by trialkylphosphines.

B) $[(R_3P)_2 \cdot (HgX_2)_2]$. In the literature, many compounds of this type are described as having the formula $R_3P \cdot HgX_2$. Evans, Mann, Peiser, and Purdie [2] showed that the molecule was double and had a bridged structure, and they considered that it probably had a tetrahedral configuration, the four groups being tetrahedrally arranged around the mercury atoms in the transposition:



$[\ (C_2H_5)_3P_2\ (HgI_2))]$ was obtained as colorless crystals, the propyl homolog was obtained both as colorless and as yellow crystals, and the butyl and amyl derivatives were obtained only in the yellow form.

The following further types of mercury complex are known:

C) $[(R_3P)_2\,(HgX_2)_3]$.
D) $[(R_3P)_2\,(HgX_2)_4]$.
E) $[(R_3P)_3\,(HgX_2)_2]$.

We have not found any data in the literature concerning complex compounds formed between full phosphorous esters and mercury halides, and we were therefore prompted to prepare such complex compounds with the object of comparing them with the phosphine complexes. We have investigated the action of mercuric chloride, bromide, and iodide on the trimethyl, triethyl, tripropyl, triisopropyl, and triphenyl esters of phosphorous acid, and have found that these mercuric halides react with the indicated esters with rise in temperature, though the triphenyl ester reacts less vigorously than the others.

Addition of one mole of mercuric salt to one mole or two moles of ester yielded products corresponding to the combination of equimolecular amounts of ester and mercury salt. The propyl and phenyl compounds were obtained in the form of thick syrups. Determination of the molecular weights by cryoscopy in benzene gave values corresponding to double molecules. Thus, the mercury complex compounds that we have prepared correspond to the phosphine complexes of type B. The physical properties of the compounds obtained are given below in a table.

All the compounds listed in the table are of low stability: they rapidly decompose on standing in air. The chloride compounds are the most stable, and the iodide compounds are the least stable. All the crystalline compounds obtained are colorless, except $[P(OC_3H_7\text{-}i)_3\,HgI_2]_2$, the crystals of which are yellow. In the preparation of the complexes $[(C_2H_5O)_3P \cdot HgCl_2]_2$ and $[(CH_3O)_3P \cdot HgCl_2]_2$, very small amounts of crystalline products having m. p. 93-96° and 114° respectively were isolated; these corresponded in phosphorus content to $(C_2H_5O)_3P \cdot 2HgCl_2$ and $(CH_3O)_3P \cdot 2HgCl_2$, respectively. It is probable that these compounds correspond in type to the type-D phosphine complexes $[(R_3P)_2(HgX_2)_4]$ but in view of the small amounts available they were not investigated further.

EXPERIMENTAL

1. Reaction of $HgCl_2$ with Trimethyl Phosphite.

Mercuric chloride (1.87 g) was added in portions to trimethyl phosphite (0.85 g, i.e., one mole per mole of

TABLE

No.	Formula	M.p. (°C)	Mol. weight	
			Found	Calculated for double formula
1	[$HgBr_2 \cdot P(OCH_3)_3]_2$, colorless cryst.	107-109	–	–
2	[$HgCl_2 \cdot P(OC_2H_5)_3]_2$, colorless cryst.	73-75 (dec.)	812.9	875.28
3	[$HgBr_2 \cdot P(OC_2H_5)_3]_2$, colorless cryst.	67-73 (dec.)	–	–
4	[$HgCl_2 \cdot P(OC_3H_{7}\text{-i})_3]_2$, colorless cryst.	117-118 (dec.)	895	959.3
5	[$HgBr_2 \cdot P(OC_3H_{7\text{-i}})_3]_2$, colorless cryst.	128-130 (dec.)	1031.2	1137.1
6	[$HgI_2 \cdot P(OC_3H_{7}\text{-i})_3]_2$, yellow cryst.	~120 (yellow cryst.)	–	–
7	$HgCl_2 \cdot P(OC_3H_7)_3$	thick liquids		
8	$HgBr_2 \cdot P(OC_3H_7)_3$			
9	$HgCl_2 \cdot (OC_6H_5)_3$	thick liquids		
10	$HgBr_2 \cdot P(OC_6H_5)_3$			

mercuric chloride). The dissolution of the salt was accompanied by evolution of heat; it did not dissolve completely. The reaction product was treated with 5 ml of dry ether (and the amount of precipitate increased). On evaporation of the ether, a small quantity of crystals, m.p. 78-84° (dec.) came down. The crystals very rapidly underwent change, forming into an oily spot on the filter paper. The product was not analyzed owing to the small amount available. The precipitate that remained after treatment of the reaction product with ether was extracted with benzene. A small quantity of colorless crystals, which melted with considerable decomposition at 114°, were obtained, and analysis for phosphorus indicated that they were composed of the addition product of two molecules of mercuric chloride with one molecule of trimethyl phosphite.

Found %: P 4.20
$C_3H_9O_3PHg_2Cl_4$. Calculated %: P 4.64

The product decomposed when left in a desiccator for four days. When heated to 240° it did not melt, but gradually sintered together.

2. Reaction of $HgBr_2$ with Trimethyl Phosphite.

Mercuric bromide (2.5 g) was added in portions to trimethyl phosphite (0.88 g). Reaction set in, the temperature rising to 53-55°. Part of the salt remained undissolved in the trimethyl phosphite. The reaction mixture was treated with a mixture of benzene and ether. A product (0.98 g) consisting of colorless prisms, m.p. 107-109° (dec.) was obtained.

Found %: P 6.52
$C_3H_9O_3PHgBr_2$. Calculated %: P 6.40

Attempts to determine the molecular weight of the product in benzene and in dioxane solution failed owing to the low solubility of the material, which crystallized out during the cooling.

3. Preparation of $HgCl_2 \cdot P(OC_2H_5)_3$

Mercuric chloride (2.44 g) was added in three portions to triethyl phosphite (1.5 g, i.e., one mole per mole of mercuric salt). With each addition, the temperature of the mixture rose to 50-53°. Scratching with a glass rod caused the reaction mass to solidify rapidly. The reaction products were extracted with a mixture of ether and benzene, giving a solution from which, on cooling, large needlelike crystals came down. The melting point after two recrystallizations was 73-75°, and the yield was 1.23 g. The portion of the reaction products that did not dissolve in the ether-benzene mixture was treated with hot benzene. When the benzene was cooled, a small quantity of crystals, m.p. 93-96° (dec.) was obtained.

Analysis of the product of m.p. 73-75°:

Found %: P 7.27; 7.00
$HgCl_2 \cdot P(OC_2H_5)_3$. Calculated %: P 7.08

Molecular weight determination:

Found: M 812.9 (cryoscopic
$HgCl_2 \cdot P(OC_2H_5)_3$. Calculated: M 437.64 method in
$[HgCl_2 \cdot P(OC_2H_5)_3]_2$. Calculated: M 875.28 benzene solution)

Analysis of the product of m.p. 93-96°

Found %: P 4.43; 4.41
$P(OC_2H_5)_3 \cdot HgCl_2 \cdot HgCl_2$. Calculated %: P 4.38

Owing to the small amount available of this substance, its molecular weight was not determined.

4. Preparation of $HgBr_2 \cdot P(OC_2H_5)_3$

The triethyl phosphite-mercuric bromide compound was prepared similarly to the previous product from 1.8 g of $HgBr_2$ and 0.8 g of the ester. Again the reaction was accompanied by evolution of heat. The solid product obtained was treated with dry ether. Some glistening crystals were isolated, but on standing in air they rapidly became dull, leaving an oily patch on the filter paper. They did not melt sharply (69-73°) (from benzene and heptane).

Found %: P 5.80; 5.99
$HgBr_2 \cdot P(OC_2H_5)_3$. Calculated %: P 5.89

5. Reaction of $HgCl_2$ with Triisopropyl Phosphite.

Expt. 1. For each mole of the ester, one mole of mercuric chloride was taken: Mercuric chloride (1.4 g) was added in small portions to triisopropyl phosphite (1 g). The mercuric chloride dissolved in the ester with rise in temperature to 42-44°. The reaction product, a gray solid mass, was extracted with benzene and then precipitated from solution by means of ligroin. The product (colorless prisms) melted, after recrystallization from methanol, at 117-118° (dec.), forming a colorless liquid, which foamed strongly and then turned milky. The product was soluble in organic solvents, but insoluble in water.

Found %: Hg 40.78; P 6.52; 6.56; Cl 15.07
$HgCl_2 \cdot P(OC_3H_7)_3$. Calculated %: Hg 41.18; P 6.46; Cl 14.79

Found: M 895 (cryoscopic
$HgCl_2 \cdot P(OC_3H_7\text{-}i)_3$ Calculated: M 479.68 method in
$[HgCl_2 \cdot P(OC_3H_7\text{-}i)_3]_2$. Calculated: M 959.36 benzene solution)

Expt. 2. Two moles of ester were taken per mole of mercuric chloride, and, after similar treatment, a product of m.p. 117-118° was isolated.

6. Reaction of $HgBr_2$ with Triisopropyl Phosphite

Mercuric bromide (1.4 g) was added in portions to triisopropyl phosphite (1.5 g). With each addition the temperature of the mixture rose to 52-55°. The reaction mixture solidified on cooling, and the product was recrystallized several times from a mixture of benzene and heptane, giving well formed, colorless prisms (0.85 g), melting with decomposition at 128-130°. It was similar in appearance to the chloride compound, but was more stable. It rapidly decomposed on standing in the air (the compound $HgBr_2 \cdot P(OC_3H_7\text{-}i)_3$ could not be recrystallized from methanol), and it was considerably more soluble than the chloride compound in ether.

Found %: P 5.30
$HgBr_2 \cdot P(OC_3H_7\text{-}i)_3$. Calculated %: P 5.44

Found: M 1031.2 (cryoscopic
$[HgBr_2 \cdot P(OC_3H_7\text{-}i)_3]$. Calculated: M 568.59 method in
$[HgBr_2 \cdot P(OC_3H_7\text{-}i)_3]_2$. Calculated: M 1137.1 benzene solution)

The product of m.p. 128-130° was prepared also by mixing one molecular proportion of $HgBr_2$ with two of triisopropyl phosphite.

7. Reaction of HgI_2 with $P(OC_3H_7\text{-}i)_3$

Mercuric iodide (0.9 g) was added gradually to triisopropyl phosphite (0.4 g, i.e., one mole per mole of mercury salt). The HgI_2 dissolved in the ester with rise of temperature (to 40°) and formation of a colorless solution, which, on being stirred with a glass rod, rapidly crystallized, forming a yellowish mass of crystals. The reaction product was dissolved in benzene, and a small amount of unchanged mercury salt was removed by filtration. Rapid evaporation of the benzene and addition of heptane led to separation of lemon-yellow needles. When heated to 120°, the product decomposed with separation of brownish material. On standing in the air the crystals changed in color, within 30 minutes of the completion of the synthesis, from lemon yellow to orange. The molecular weight of the compound was not determined owing to its instability.

Found %: P 4.40
$HgI_2 \cdot P(OC_3H_7\text{-}i)_3$. Calculated %: P 4.67

The phenyl ester of phosphorous acid reacted very feebly with $HgCl_2$ and $HgBr_2$. After the usual solvent treatments, attempts to isolate crystalline compounds failed.

The n-propyl ester of phosphorous acid reacted very vigorously with $HgCl_2$ and $HgBr_2$, but the reaction products did not crystallize, but remained in the form of a thick syrup.

SUMMARY

1. It has been found that mercuric halides react with full esters of phosphorous acid with formation of complex compounds. The following compounds have been isolated in the crystalline form:

$[HgBr_2 \cdot P(OCH_3)_3]_2$; $[HgCl_2 \cdot P(OC_2H_5)_3]_2$.
$[HgBr_2 \cdot P(OC_2H_5)_3]_2$; $[HgCl_2 \cdot P(OC_3H_7\text{-}i)_3]_2$.
$[HgBr_2 \cdot P(OC_3H_7\text{-}i)_3]_2$; $[HgI_2 \cdot P(OC_3H_7\text{-}i)_3]_2$.

2. Molecular weight determinations by cryoscopy in benzene on the compounds formed showed that their molecules are dimeric.

3. The complex compounds obtained, complexes of mercuric halides with trialkyl phosphites $[(RO)_3P \cdot HgX_2]_2$, are analogs of the corresponding phosphine complexes $[R_3P \cdot HgX_2]_2$, and they belong to the bridged type.

LITERATURE CITED

[1] A. E. Arbuzov and V. M. Zoroastrova, Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci., No. 5, 818 (1952).*

[2] R. C. Evans, F. G. Mann, H. S. Peiser and D. Purdie, J. Chem. Soc. 1209 (1940).

Received June 23, 1952

A. M. Butlerov Chemical Research Institute
of the V. I. Ulyanov-Lenin Kazan State University

---

* See Consultants Bureau translation, p. 737.

THE TAUTOMERISM OF CARBOSTYRIL DERIVATIVES

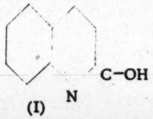
A. E. Arbuzov and M. Sh. Bastonova

The discovery of the tautomerism of carbostyril derivatives is of long standing, being comparable in this respect to similar discoveries concerning the tautomerism of acetoacetic ester and isatin, and the behavior of carbostyril and its derivatives is regarded as a classical, deeply studied example of tautomeric phenomena. However, examination of the literature shows that the question of the tautomerism of carbostyril and its derivatives has not, in fact, received adequate study [1, 3, 4], and the structure of carbostyril, as also that of isatin, cannot be considered to be unequivocally established.

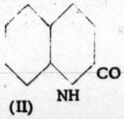
In our previous communication [2], the tautomerism of isatin derivatives was considered, and the main questions that arose — which concerned the structures of the tautomeric compounds themselves, the structures of their metal derivatives, and the double-decomposition reactions of the metal derivatives of the tautomers with halogen compounds — may be associated in equal measure with carbostyril derivatives. The only difference is that the matter is still more complicated for carbostyril.

The establishment of the existence of two series of derivatives, regarded as O- and N-derivatives, occurred somewhat later (in 1887) for carbostyril than for isatin [4]. Whereas the action of methyl (or ethyl) iodide on the silver salt leads to the formation of the O-methyl (or O-ethyl) ether, reaction of these halides with alkaline solution of carbostyril gives N- and O-alkyl-substituted carbostyrils in various relative amounts, depending on the reaction conditions.

Carbostyril itself, as also isatin, has been obtained only in one form, but, since it forms two series of derivatives, regarded as O- and N-derivatives, it may be assigned two formulas, I and II:



(I)



(II)

The structures of the alkyl esters of carbostyril were established on the basis of hydrolysis reactions, it being shown that some of these esters, the N-derivatives, were stable to the action of dilute mineral acids, whereas others, the O-derivatives, were hydrolyzed with formation of carbostyril; also, the latter are converted into N-derivatives by treatment with alkyl halide.

In the present communication, results are given of a study of double-decomposition reactions of the sodium, potassium and silver salts of carbostyril with certain halogen compounds, including halogen-substituted ethers. The alkali salts of carbostyril were prepared by the action of metallic sodium on a solution of carbostyril in freshly prepared absolute alcohol, and the silver salt was prepared from a 1% aqueous solution of carbostyril and silver nitrate solution by addition of ammonia. The salts were preserved in a desiccator, and, before being used for the reaction, the alkali salts were given a careful supplementary drying treatment. A study was made of the reactions of the carbostyril salts with the following aralkyl halides, which were prepared by the usual methods: benzyl bromide and chloride, α-bromo-p-xylene, bromotriphenylmethane, and chlorotriphenylmethane.

The reactions with the following halogen-substituted ethers were studied also: bromomethyl methyl ether, chloromethyl methyl ether, bromomethyl ethyl ether, chloromethyl ethyl ether, bromomethyl propyl ether, and chloromethyl propyl ether. All the starting materials were taken in a freshly prepared condition for reaction. The reactions were carried out in a medium of dry ether or of benzene under varying conditions of temperature: normal temperature, at the boiling point of the solvent, or at higher temperature in a sealed tube.

By the action of bromomethyl methyl ether and of chloromethyl methyl ether on the silver salt of carbostyril, and carbostyril methoxymethyl ether, m.p. 66-67°, was isolated in each case; by the action on the silver salt of the bromomethyl and of the chloromethyl ethyl ethers, a carbostyril ethoxymethyl ether, m.p. 39-40°, was isolated; and from the bromomethyl and chloromethyl propyl ethers and the silver salt, a carbostyril propoxymethyl ether, b.p. 192-193°/12 mm, was isolated. Experiments carried out with bromomethyl and chloromethyl methyl ethers and the potassium and sodium salts of carbostyril did not lead to the preparation of a carbostyril methoxymethyl ether; carbostyril itself was obtained in all cases, owing, probably, to the exceptional readiness with which the ether obtained is hydrolyzed.

The methoxymethyl and ethoxymethyl ethers of carbostyril consist of white, well formed, needlelike crystals, but the propoxymethyl ether is a colorless liquid. All the compounds are of good solubility in ether and in benzene.

Hydrolysis of carbostyril methoxymethyl ether in caustic potash solution at the boil for one hour led to formation of carbostyril (in almost theoretical yield) and formaldehyde, which was detected by a qualitative reaction.

Attempts to hydrolyze the ethoxymethyl and propoxymethyl ethers of carbostyril in a 10% solution of caustic alkali gave negative results: the substances remained unchanged. By heating bromomethyl methyl ether with carbostyril methoxymethyl ether, a high-melting product was obtained. An attempt to hydrolyze carbostyril propoxymethyl ether in a 10% solution of hydrochloric acid also gave a negative result. The propoxymethyl ether, on being heated at 140-150° for two hours, yielded a high-melting product.

By the action of bromotriphenylmethane and of chlorotriphenylmethane on the silver and sodium salts of carbostyril, the same product was obtained in all cases: (triphenylmethyl)carbostyril, m.p. 180-181°, in the form of colorless crystals, readily soluble in ether and in benzene.

Hydrolysis of (triphenylmethyl)carbostyril in caustic potash solution yielded carbostyril and triphenylmethanol in almost quantitative yield.

By the action of benzyl bromide and of benzyl chloride on the silver salt and on the sodium salt of carbostyril, different substances were obtained (judging from their melting points). Thus, by the action of these halogen compounds on the silver salt of carbostyril, a benzylcarbostyril, of m.p. 50-51° was obtained, whereas by their action on the sodium or potassium salt a benzylcarbostyril of m.p. 95-96° was formed.

By the action of α-bromo-p-xylene on the silver salt and on the sodium salt of carbostyril, (p-tolylmethyl) carbostyrils of different melting points were obtained, as in the case of the benzyl compounds. By the action of α-bromo-p-xylene on the silver salt of carbostyril, a (p-tolylmethyl)carbostyril of m.p. 71-72° was obtained, and by its action on the sodium salt a (p-tolylmethyl)carbostyril of m.p. 131-132° was formed. Both benzylcarbostyrils and also both (p-tolylmethyl)carbostyrils were found to be very stable compounds and were not hydrolyzed when heated with 10% caustic alkali solution; on the other hand, when heated with 10% acid, the benzylcarbostyril and (p-tolylmethyl)carbostyril that had been prepared from the silver salt of carbostyril were hydrolyzed with formation of carbostyril.

The benzylcarbostyril and (p-tolylmethyl)carbostyril that were prepared from the silver salt of carbostyril and had the lower melting points (51° and 72°) are converted by being heated with benzyl bromide and α-bromop-p-xylene respectively into the corresponding compounds of higher melting point (96° and 132°).

Since the benzyl and p-tolylmethyl ethers of carbostyril have each been obtained in two forms, one of which may be converted into the other, their molecular weights were determined. The estimation was done by Rast's method, and it gave values corresponding to monomolecular products.

EXPERIMENTAL

Preparation of Carbostyril Methoxymethyl Ether

Action of bromomethyl methyl ether on the silver salt of carbostyril. The silver salt of carbostyril (1.26 g) was added to a solution of bromomethyl methyl ether (0.95 g) in dry ether (15 ml). Reaction set in very quickly and proceeded with evolution of heat (the ether boiled). After 30 minutes the solution was filtered and the residue was washed with dry ether. When the ether had been driven off, a thick, oily liquid remained, and this was distilled under a pressure of 17 mm Hg (b.p. 172-175°). The substance obtained (0.7 g, 50%) crystallized after standing for some time yielding white needles of m.p. 66-67°.

In a second experiment 1.25 g of bromomethyl methyl ether and 2.52 g of the silver salt were taken, and the reaction was carried out in a dry benzene medium, the mixture being heated for 30 minutes at the boil. A white substance (1.73 g, 90.1%) in the form of small needles separated from the benzene solution; it melted at 66-67°.

Analysis of the substance of m.p. 66-67°:

Found %: N 7.66
$C_{11}H_{11}NO_2$. Calculated %: N 7.41

The methoxymethyl ether has a pleasant odor and is of good solubility in ether, benzene, and alcohol.

Action of chloromethyl methyl ether on the silver salt of carbostyril. The silver salt of carbostyril (2.52 g) was added to a solution of chloromethyl methyl ether (0.81 g) in dry benzene (15 ml). The reaction was carried out at the boiling point of benzene. After separation of silver chloride, the benzene solution was placed under vacuum. The residual oily liquid crystallized out when cooled with snow. The product (1.28 g, 68%) melted at 66-67°.

Found %: N 7.69
$C_{11}H_{11}NO_2$. Calculated %: N 7.41

Action of bromomethyl methyl ether on the sodium salt of carbostyril. Experiments were carried out under various conditions: at the boiling point of benzene, in a sealed tube heated in a boiling water bath, in a sealed tube at 110-115°, and in a sealed tube at 140-150°. The sodium salt used was carefully dried prior to the reaction. In no case was a carbostyril methoxymethyl ether isolated, but carbostyril was obtained, either in traces, or in larger amount.

The materials sealed in the tube were: bromomethyl methyl ether (1.25 g), dry benzene (10 ml), and the sodium salt (1.67 g). Heating was carried out at 110-115°. From the benzene solution, 0.9 g of carbostyril, m.p. 198-199°, was obtained.

Action of bromomethyl methyl ether on the potassium salt of carbostyril. Two experiments, at the boiling point of benzene and at 110-115°, were carried out. In each experiment carbostyril was obtained.

The flask contained bromomethyl methyl ether (1.25 g), dry benzene (15 ml), and the potassium salt (1.93 g). Reaction set in fairly quickly and proceeded with evolution of heat (the temperature rose to 40°). The mixture was boiled on the bath for 30 minutes and was filtered while still hot, the residue being washed by warming with dry benzene. The amount of potassium bromide obtained was 1.08 g (calculated amount: 1.09 g). The benzene solution yielded 1.36 g of a substance of m.p. 194-196° which melted after recrystallization from alcohol at 198-199° (i.e., it was carbostyril).

Bromomethyl methyl ether (1.25 g), dry benzene (10 ml), and the potassium salt (1.93 g) were heated together in a sealed tube at 110-115° for one hour. Carbostyril (0.82 g), m.p. 198-199°, was isolated from the benzene solution.

Preparation of Carbostyril Ethoxymethyl Ether

Action of bromomethyl ethyl ether on the silver salt of carbostyril. The silver salt of carbostyril (1.26 g) was added to a solution of bromomethyl ethyl ether (1.38 g) in dry ether (20 ml). Reaction set in very rapidly, heat being evolved (the ether boiled). The reaction mixture was boiled for 30 minutes and then filtered under suction, the residue being washed several times with dry ether. The ether was driven off,, and a precipitate (1.1 g) formed in the solution. It was treated with water (20 ml), and part of it remained undissolved as an oil at the bottom of the flask. When the mixture was filtered , the oily part remained on the filter paper; it gave a negative result in Beilstein's test for halogen. The oil was transferred to a watch glass and, after two hours, needlelike crystals (0.12 g) of m.p. 39° separated out in fan formation. The oil remaining on the filter paper was extracted with ether, and from the ethereal solution a further 0.32 g of substance of m.p. 39.5-40° was isolated. The total yield was therefore 0.5 g (50%). The substance obtained was of good solubility in ether, benzene, and alcohol, but was insoluble in water.

Found %: N 7.92
$C_{12}H_{13}ON$. Calculated %: N 7.48

Action of chloromethyl ethyl ether on the silver salt of carbostyril. The silver salt (0.9 g) was added to a solution of chloromethyl ethyl ether (0.4 g) in dry benzene (15 ml). Reaction set in and was accompanied by some evolution of heat, the temperature rising nearly to the boiling point of benzene. The mixture was heated at the boiling point of benzene for 30 minutes, and the solution was then filtered off under suction. A viscous liquid (0.9 g) remained after removal of the benzene; it was poured onto a watch glass, which was placed on snow. After one day the substance began to crystallize; the crystals that separated were pressed off between filter papers, and 0.4 g (56%) of a substance of m.p. 39-39.5° was obtained. In admixture with the substance obtained by the reaction of bromomethyl ethyl ether with the silver salt of carbostyril, it melted at 38.5-39.5°.

Found %: N 6.89
$C_{12}H_{13}ON$. Calculated %: N 7.48

Found %: N 7.15
$C_{12}H_{13}ON$. Calculated %: N 7.48

Preparation of Carbostyril Propoxymethyl Ether

Action of bromomethyl propyl ether on the silver salt of carbostyril. The silver salt (2.52 g) was added to bromomethyl propyl ether (1.52 g) dissolved in dry ether (15 ml). Reaction set in very quickly, and it proceeded with evolution of heat (the ether boiled). The reaction mixture was heated at the boiling point of ether (on a water bath) for 30 minutes, and the solution was then filtered off under suction. In the distillation flask, after the ether had been driven off, there remained a viscous liquid, which was vacuum-distilled (b.p. 192-193°/12 mm in this and also in a further distillation). It had a sharp odor, similar to that of the substance obtained by reaction with chloromethyl propyl ether. The substances obtained in the reactions of the silver salt of carbostyril with bromomethyl and with chloromethyl propyl ether were united and distilled. The boiling point of the mixture was not lower than that of its components.

Found %: N 6.90
$C_{13}H_{15}ON$. Calculated %: N 6.96

Action of chloromethyl propyl ether on the silver salt of carbostyril. The silver salt (2.27 g) was added to a solution of chloromethyl propyl ether (1.0 g) in dry benzene (15 ml). Reaction started when the mixture was heated to boiling, and heating was continued at this temperature for 45 minutes. The benzene solution was distilled, and a viscous liquid remained, which distilled over at 196-197° under 15 mm pressure. The yield was 0.95 g (calculated amount: 1.92 g). The substance had a sharp characteristic odor.

Found %: N 6.78
$C_{13}H_{15}ON$. Calculated %: N 6.96

Preparation of (Triphenylmethyl) carbostyril

Action of bromotriphenylmethane on the silver salt of carbostyril. The silver salt of carbostyril (1.26 g) was added to a solution of bromotriphenylmethane (1.6 g) in dry benzene (15 ml). Reaction set in very quickly. A white crystalline substance (1.9 g) of m.p. 176-178° separated from the benzene solution when a part of the solvent had been driven off. After recrystallization from dry benzene, the substance melted at 180-181°.

Found %: N 3.69
$C_{28}H_{21}ON$. Calculated %: N 3.62

Action of chlorotriphenylmethane on the silver salt of carbostyril. The silver salt of carbostyril (1.26 g) was added to a solution of chlorotriphenylmethane (1.39 g) in dry benzene (15 ml). The mixture was maintained at its boiling point during the reaction. Crystals of m.p. 167-171° separated from the benzene solution; after several recrystallizations they melted at 180-181°. In admixture with those obtained in the preceding experiment, they melted at 180-181.5°.

Found %: N 3.69
$C_{28}H_{21}ON$. Calculated %: N 3.62

Action of bromotriphenylmethane on the sodium salt of carbostyril. The sodium salt of carbostyril (0.9 g) was added to a solution of bromotriphenylmethane (1.6 g) in benzene (10 ml). Heating was applied, and the reaction went very quickly. A fine precipitate, m.p. 176-180°, came down from the benzene solution. By fractional crystallization from the benzene solution obtained after the extraction of the sodium bromide, triphenylmethanol (0.45 g; well defined octahedral crystals melting at 156-160°, alone and in admixture with pure triphenylmethanol) and carbostyril (0.15 g; m.p. 198-199° after recrystallization from alcohol) were isolated.

Action of chlorotriphenylmethane on the sodium salt of carbostyril. The sodium salt of carbostyril (0.84 g) was added to a solution of chlorotriphenylmethane (1.39 g) in dry benzene (15 ml), and the mixture was heated for 30 minutes. Triphenylmethanol (0.42 g; m.p. 159-160°) and carbostyril (0.5 g; m.p. 196-198°) were isolated from the benzene solution.

Preparation of Benzylcarbostyril

Action of benzyl bromide on the silver salt of carbostyril. The silver salt of carbostyril (2.54 g) was added to a solution of benzyl bromide (1.7 g) in dry benzene (15 ml), and the mixture was heated at the boiling point of benzene for one hour. The precipitate of silver bromide was separated from the benzene solution, and the benzene was driven off. There remained a viscous, oily liquid, from which, after standing in snow, a crystalline substance (2.41 g) in the form of thick needles came down. The precipitate, after being recrystallized three times from alcohol, melted at 50-51°; the amount obtained was 1.46 g (62 %).

Found %: N 5.64

$C_{16}H_{13}NO$. Calculated %: N 5.96

Action of benzyl chloride on the silver salt of carbostyril. The silver salt of carbostyril (1.26 g) was added to a solution of benzyl chloride (0.64 g) in dry benzene (15 ml). The conditions of the reaction were similar to those in the previous experiment. A substance (0.18 g) of m.p. 50-51° was obtained from the benzene solution.

Action of benzyl bromide on the sodium salt of carbostyril. Benzyl bromide (0.93 g), dry ether (13 ml), and the sodium salt of carbostyril (0.91 g), were sealed in a tube and heated for two hours at 140-150° and for two hours at 160-170°. When the contents of the tube had cooled, they were filtered. The ether was driven off, and there remained a thick, oily, slightly yellowish liquid, which was vacuum-distilled (b.p. about 170° at 17 mm). It crystallized on standing, giving thick white needles, m.p. 95-96.5°. It had a rather unpleasant odor.

Action of benzyl chloride on the sodium salt of carbostyril. Benzyl chloride (1.8 g), dry ether (20 ml), and the sodium salt of carbostyril (2.5 g) were sealed in a tube and heated for four hours at 150-170°. When the contents of the tube had cooled, they were filtered, and from the solution, after removal of the ether, a viscous, slightly yellowish oil was obtained; it was vacuum-distilled, and it then crystallized rapidly (1.1 g, 32.7%; m.p. 95-96.5°).

Found %: N 6.08

$C_{16}H_{13}NO$. Calculated %: N 5.96

Action of benzyl bromide on the potassium salt of carbostyril. Benzyl bromide (0.71 g), dry ether (15 ml), and the potassium salt of carbostyril (1.83g) were sealed in a tube and heated for four hours at 150-170°. The potassium bromide was separated and the ether driven off, and there remained a thick oily liquid, which crystallized in needles, m.p. 94-95° (95-96° after recrystallization from alcohol). The yield was 0.62 g (26.38%); 0.18 g of the potassium salt remained unchanged. The melting point of a mixture of this substance with benzylcarbostyril obtained by the action of benzyl chloride on the sodium salt of carbostyril was 94-95°.

Preparation of (p-Tolylmethyl)carbostyril

Action of α-bromo-p-xylene on the silver salt of carbostyril. The silver salt of carbostyril (2.4 g) was added to a solution of α-bromo-p-xylene (1.78 g) in dry benzene (15 ml), and the mixture was heated at the boiling point of benzene for one hour. The benzene was driven from the solution, and a thick, oily liquid remained. This was stood in snow, and an amorphous substance (1.1 g, 50%) of m.p. 67-72° was precipitated; the melting point after recrystallization from alcohol was 71-72°. In another experiment, in which larger amounts of starting materials were used (3.05 g of α-bromo-p-xylene and 3.92 g of the silver salt), (p-tolylmethyl)carbostyril was obtained in 94% of the theoretical yield (3.76 g).

Found %: N 5.86

$C_{17}H_{15}ON$. Calculated %: N 5.62

Action of α-bromo-p-xylene on the sodium salt of carbostyril. The sodium salt of carbostyril (0.85 g) was added to a solution of α-bromo-p-xylene (0.8 g) in dry ether (10 ml). The reaction was carried out in a sealed tube at 165-170° for two hours. The tube was opened on the next day. After evaporation of the ether, the solution yielded needlelike crystals, m.p. 106-108°. After recrystallization from alcohol the melting point rose to 131-132°. The yield was 0.8 g (73%).

Found %: N 5.92

$C_{17}H_{15}ON$. Calculated %: N 5.62

Hydrolysis Experiments

Hydrolysis of (triphenylmethyl)carbostyril. An excess of caustic potash (5 g) was added to (triphenylmethyl) carbostyril (0.2 g) contained in a small flask, and the mixture was heated for 30 minutes over a gauze. The substance did not go into solution, but formed a voluminous precipitate, which was filtered off under suction and washed until all alkali had been removed. The material obtained (0.2 g; m.p. 142-170°) was shaken with dilute hydrochloric acid, filtered, washed until neutral reaction was obtained, and extracted with ether, when a fairly considerable amount of the substance remained undissolved. The ether solution yielded a substance of m.p. 150-155°, and after further recrystallizations from ether it melted at 160-162°. The yield was 0.11 g (84.6%). In admixture with authentic triphenylmethanol it melted at 160-161°. The ether-insoluble substance was recrystallized from alcohol. The melting point after three recrystallizations was 198-199°. The yield was 0.04 g (92.0%).

TABLE

Hydrolysis of Benzylcarbostyril and of (p-Tolylmethyl)carbostyril in presence of alkali

Expt. No.	Amount of substance taken for hydrolysis	10% KOH taken (ml)	Duration and temperature of heating	Amt. obtained after neutralization with H_2SO_4, extraction with ether, and recrystallization from alcohol.
	Of benzylcarbostyrils:			
1	0.3 g of m.p. 95-96°	10	1 hr. on water bath and 1 hr. over gauze at the boil	0.26 g of m.p. 95-96°
2	0.4 g of m.p. 50-51°	10		0.3 g of m.p. 50-51°
3	0.18 g of m. p. 95-96°	4	1 hr. at 145-150°	0.15 g of m.p. 96-97°
4	0.4 g of m.p. 50-51°	6	1 hr. at 150-160°	0.33 g of m.p. 51°
	Of (p-tolylmethyl)carbostyrils:•			
5	0.24 g of m.p. 71°	10	1 hr. over gauze at the boil	0.24 g of m.p. 71°
6	0.3 g of m.p. 132°	10		0.3 g of m.p. 131-132°
7	0.3 g of m.p. 71°	4	1 hr. at 150-160°	0.3 g of m.p. 71-71.5°
8	0.24 g of m.p. 131-132°	4	1 hr. at 150-160°	0.24 g of m.p. 132°

• In every experiment the substance taken remained undissolved: it melted and settled on the bottom of the flask or tube. After the treatment, the substances were recrystallized from alcohol and yielded needlelike crystals.

Hydrolysis in presence of hydrochloric acid of the benzylcarbostyril obtained from the silver salt of carbostyril. A mixture of the benzylcarbostyril of m.p. 48.5-50° (0.5 g) and a 10% solution of hydrochloric acid (10 ml) was heated in a sealed tube for 40 minutes at 140-155° and for one hour at 155-160°. When the tube was opened, there was a strong odor of benzyl alcohol. From the aqueous solution, when cool, well formed white needles, m.p. 191°, came down (0.1 g). Apart from the crystals, some resinous material (0.39 g) was separated, and, when this was boiled with water, a further 0.06 g of carbostyril, m.p. 191-193°, was separated. Thus, the total yield of carbostyril was 0.16 g (50%). The melting point of a mixture with pure carbostyril was 196°.

Hydrolysis in presence of hydrochloric acid of the (p-tolylmethyl)carbostyril obtained from the silver salt of carbostyril. A mixture of the (p-tolylmethyl)carbostyril of m.p. 72° (0.25 g) and a 10% solution of hydrochloric acid (6 ml) was heated in a sealed tube for one hour at 130-140° and for one hour at 140-148°. From the aqueous solution, when cool, 0.05 g (30%) of carbostyril was isolated, but not all the carbostyril formed was accounted for quantitatively. A second experiment on 0.5 g of (p-tolylmethyl)carbostyril under the same conditions yielded 0.21 g (78 %) of carbostyril. In each case, when the tube was opened, there was a strong odor reminiscent of the odor of aromatic alcohols.

Hydrolysis of carbostyril methoxymethyl ether. A 10% solution of caustic potash (10 ml) was added to carbostyril methoxymethyl ether (1.28 g), and the mixture was heated at the boil for one hour. The solution was neutralized with sulfuric acid, and needlelike crystals came down. At the same time, a smell of formaldehyde was noted, and the presence of the substance in the aqueous solution was detected by a qualitative reaction. The precipitate, filtered off and washed with water, had m.p. 160-175°. It melted, after recrystallization from alcohol, at 198-199°; the yield was 0.8 g (81.5%).

Attempted hydrolysis of carbostyril ethoxymethyl ether. A mixture of the substance (0.2 g) with 10% caustic potash (10 ml) was heated in a small flask for 90 minutes. The solution was neutralized to a weakly acid reaction and extracted with ether. The extract, after evaporation of the ether, yielded 0.1 g of crystals in a fan array; they melted at 40°.

Attempted hydrolysis of carbostyril propoxymethyl ether. Expt. 1. A 0.1 N solution of caustic potash (25 ml) was added to the substance (0.7 g), and the mixture was heated under reflux in a small flask for one hour. The solution was cooled and neutralized with sulfuric acid to a weakly acid reaction. An oily substance and a small amount of white precipitate came out of the solution and were filtered off. The substance remaining on the filter (0.06 g) melted at 177-192°; it appeared to be dirty and heterogeneous. After evaporation of water from the solution, an oily substance (0.6 g) separated out, and this did not crystallize after standing for about a month. It was readily soluble in ethanol, and it separated again from its solution in ethanol, when the latter was evaporated off, as a thick yellowish oil.

Expt. 2. A 10 % solution of caustic potash (3 ml) was added to the substance to be treated (0.5 g). The mixture was heated in a sealed tube at 147-150° for one hour. When the tube was cooled, the same amount of oily liquid separated as had been taken for the hydrolysis treatment. The contents of the tube were poured into a beaker, and the solution was neutralized with 10% hydrochloric acid, when a precipitate of dirty flocculent material was formed. The solution was heated on the hotplate at the boil for 15 minutes; the precipitate did not disappear, and the oily component did not diminish in volume. The whole was then filtered, and the oil and the precipitate remained on the filter. Part of the oily material was absorbed by the filter, and a part (0.15 g) remained on the filter in the form of a cream-colored paste, which was only slightly soluble in alcohol. From the aqueous solution, after evaporation of the water, an insignificant white residue was obtained; this darkened on being heated to above 250°, and did not melt, even at 305°.

It was concluded that carbostyril propoxymethyl ether is not hydrolyzed when heated with a 10% solution of caustic potash at 150° for one hour.

Attempt to hydrolyze carbostyril propoxymethyl ether with a 10% solution of hydrochloric acid. Carbostyril propoxymethyl ether (1.45 g) and a 10% solution of hydrochloric acid, (10 ml) were heated together in a sealed tube at 140-150° for two hours. There was no excess pressure in the tube when it was opened, but an ethereal odor was noted. From the solution, when cooled, flocculent material was precipitated, and this was filtered off and washed with water. The ethereal odor of the solution gradually became less marked; finally, after the solution had stood for a long time, the odor disappeared. The flocculent precipitate was canary yellow in color. On being heated (melting point determination), it began to darken at 180° and did not melt below 240°. It was recrystallized from alcohol. Again it did not melt: at above 200° it began to darken somewhat, turning from canary yellow to beige, and at 295° a small amount of liquid appeared in the capillary, but the substance did not melt completely even at 300°. The precipitate was only partly dissolved in alcohol for the purpose of recrystallization, but the precipitate as a whole presented much the same picture as that presented by the recrystallized part.

Thus, 0.23 g of recrystallized material was obtained (it was white at first, but became canary yellow again on standing), and 0.5 g of a somewhat more grayish material remained; in the melting point test, the latter began to darken at above 230° and melted at 260-280°. This substance was insoluble in water and did not readily dissolve in alcohol. It separated from its alcoholic solution in the form of a flocculent precipitate. A Beilstein test for halogen gave a negative result. The aqueous solution was neutralized, and a qualitative test for aldehyde (ammoniacal silver nitrate solution) was made; it gave a negative result.

Isomerization Experiments

Action of benzyl bromide on benzylcarbostyril. Benzyl bromide (0.22 g) was added to benzylcarbostyril of m.p. 50-51° (0.36 g) contained in a tube having a constriction. The tube was sealed and was heated for one hour at 145-150° and for one hour at 150-160°. The tube was cooled, and it was found that the liquid had diminished somewhat in volume and had become darker in color. Excess benzyl bromide was driven off under reduced pressure, and the residual solution was cooled in snow. White crystals separated, and they were recrystallized three times from alcohol (0.15 g; m.p. 94-95°). A mixture of this substance and the substance obtained by the action of benzyl chloride on the sodium salt of carbostyril melted at 95-96°

Action of α-Bromo-p-xylene on (p-tolylmethyl) carbostyril. α-Bromo-p-xylene (0.28 g) and dry ether

(1.5 ml) were added to (p-tolylmethyl)carbostyril of m.p. 71° (0.4 g) contained in a tube having a constriction. The tube was sealed and was heated for two hours at 170-190°. The tube was cooled and opened, and the contents were poured out into a crystallizing dish. A substance that appeared to be impure and was mixed with α-bromo-p-xylene was precipitated from the ether solution. It was pressed off between small pieces of filter paper, and was recrystallized from anhydrous ethanol. The melting point after recrystallization was 128-130°. A mixture of this substance with the substance (m.p. 131°) obtained from the sodium salt of carbostyril and α-bromo-p-xylene melted at 130-131°.

Action of bromomethyl methyl ether on carbostyril methoxymethyl ether. The methoxymethyl ether of m.p. 66-67° (0.4 g) and bromomethyl methyl ether (1.2 g) were sealed in a tube having a constriction and heated for one hour at 110-120°. After being heated, the solution was darker in color. The contents of the tube were poured out into a crystallizing dish, and a substance separated which, after several washes with ether, melted at 160-190°. This substance was almost insoluble in ether and in benzene; it dissolved readily in alcohol, but did not separate out again. By recrystallization from mixed solvents – alcohol and ether – it was obtained as a white powder, which in the melting-point test began to darken at 200°, had blackened almost completely at 220°, and melted at 223-226°.

SUMMARY

1. By the action of bromomethyl methyl ether, of chloromethyl methyl ether, of bromomethyl ethyl ether, of chloromethyl ethyl ether, of bromomethyl propyl ether, and of chloromethyl propyl ether on the sodium and silver derivatives of carbostyril, the corresponding ethers were obtained:

Carbostyril methoxymethyl ether, m.p. 66-67°
Carbostyril ethoxymethyl ether, m.p. 39-40°
Carbostyril propoxymethyl ether, b.p. 192-193° at 12 mm.

2. On hydrolysis, carbostyril methoxymethyl ether gave carbostyril (in almost quantitative yield) and formaldehyde.

3. The ethoxymethyl and propoxymethyl derivatives of carbostyril do not undergo hydrolysis in dilute alkali or acid. This has been confirmed in repeated experiments. When the propoxymethyl derivative was heated with dilute acid at 140-150°, a high-melting product was obtained.

4. By the action of chlorotriphenylmethane, of benzyl bromide and chloride, and of α-bromo-p-xylene on the sodium and silver derivatives of carbostyril the following products were obtained: (triphenylmethyl) carbostyril of m.p. 180-181°; benzylcarbostyril in two forms of m.p. 50-51° and 95-96° respectively; and (p-tolylmethyl)carbostyril in two forms of m.p. 71-72° and 131-132° respectively.

5. On hydrolysis, (triphenylmethyl)carbostyril gave triphenylmethanol and carbostyril in almost quantitative yields.

6. Attempts to hydrolyze the two forms of benzylcarbostyril and the two forms of (p-tolylmethyl)carbostyril in dilute alkali did not give positive results. They were hydrolyzed in dilute acid, yielding carbostyril.

7. The sodium and potassium salts of carbostyril gave identical products when they reacted with benzyl bromide (or chloride); they gave identical products also when they reacted with bromomethyl methyl ether (or chloromethyl methyl ether).

8. An attempt to isomerize the methoxymethyl derivative of carbostyril in presence of bromomethyl methyl ether led to the formation of a high-melting product.

9. The lower-melting forms of benzylcarbostyril and (p-tolylmethyl)carbostyril were found to be isomerized when heated with the corresponding aralkyl halides into the higher-melting forms of these substances.

LITERATURE CITED

[1] A. E. Arbuzov, Bull. Acad. Sci., U.S.S.R., 211 (1939). [2] A. E. Arbuzov and M. Sh. Bastanova, Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci., No. 3, 459 (1952).* [3] R. Friedlander and Ostermajer, Ber. 15, 333, 335, 337 (1882); R. Friedlander and Weinberg, Ber., 15, 1421, 2103 (1882); 18, 1528 (1885). [4] R. Friedlander and F. Muller, Ber. 20, 2009 (1887).

Received June 23, 1952

S.M. Kirov Kazan Chemical and Technological Institute

---

* See Consultants Bureau translation, p. 443.

ACTION OF ALKYL HALIDES ON SODIUM, POTASSIUM, AND SILVER DIALKYL PHOSPHOROTHIOATES

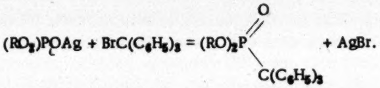
A. E. Arbuzov and O. M. Shapshinskaya

Investigation of addition reactions of "dialkylphosphorous acids" (dialkyl hydrogen phosphites or dialkyl phosphonates – Translator) has played a very important part in the study of their structure [1]. Our study of the addition of sulfur to salts of dialkylphosphorous acids, carried out in 1949-1950 [2], led us to the preparation of the corresponding metal dialkyl phosphorothioates, and we prepared sodium, potassium, and silver dialkyl phosphorothioates having ethyl, propyl, isopropyl, and butyl as alkyl radicals. Sodium, potassium, and silver dialkyl phosphorothioates are crystalline substances having definite constants.

A. E. Arbuzov and his coworkers [3,4] made a systematic study of the double-decomposition reaction between the metal derivatives of dialkylphosphorous acids and halogen derivatives of various alkanes, aranes, and organic acids. The results of these reactions varied greatly. For example, whereas the reaction between silver dialkylphosphite and chlorotriphenylmethane went according to the equation

$$(RO)_2POAg + ClC(C_6H_5)_3 = (RO)_2POC(C_6H_5)_3 + AgCl,$$

the reaction between silver dialkylphosphite and bromotriphenylmethane, on the other hand, followed the equation



$$(RO_2)POAg + BrC(C_6H_5)_3 = (RO)_2P(=O)C(C_6H_5)_3 + AgBr.$$

The reaction with the silver salt of diisopropylphosphorous acis is an exception – in this case the reaction follows the previous equation, i.e., a mixed ether being obtained. The reaction between copper salts of dialkylphosphorous acid and triphenylmethyl chloride follows the equation:

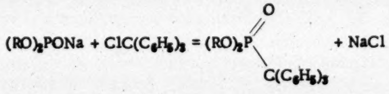
$$(RO)_2POCu + ClC(C_6H_5)_3 = (RO)_2POC(C_6H_5)_3 + CuCl.$$

The reaction between copper salts of a dialkylphosphorous acid and triphenylmethyl bromide follows the equation:

$$2(RO)_2POCu + 2BrC(C_6H_5)_3 = [(RO)_2PO]_2 + 2(C_6H_5)_3C + 2CuBr,$$

i.e., with formation of free radicals.

The reaction between chlorotriphenylmethane and the alkali salts goes according to the equation



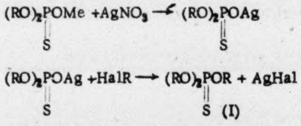
$$(RO)_2PONa + ClC(C_6H_5)_3 = (RO)_2P(=O)C(C_6H_5)_3 + NaCl$$

and the reaction of bromotriphenylmethane and other bromotriarylmethanes with the alkali salts (Li, K, Na, Rb, Cs) of dialkylphosphorous acids proceeds with formation of free radicals:

$$2(RO)_2POMe + 2BrC(C_6H_5)_3 = [(RO)_2PO]_2 + 2(C_6H_5)_3C + 2MBr.$$

Thus, it is clear that the course of the reaction between metal derivatives of dialkylphosphorous acids and halogen compounds depends on the nature of the metal, the nature of the halogen, and the structure of the organic radical. Having obtained sodium, potassium, and silver dialkyl phosphorothioates, we set ourselves the task of studying the effects of the nature of the metal and of the halogen in the reaction between the metal dialkyl phosphorothioates and the corresponding alkyl halides with formation of the corresponding trialkyl phosphorothioates.

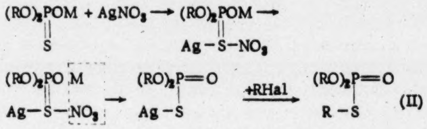
When alkyl halides react with silver dialkyl phosphorothioates, the reaction of ester formation may proceed in the following directions: either to give I:



$$(RO)_2\underset{\underset{S}{\|}}{P}OMe + AgNO_3 \rightarrow (RO)_2\underset{\underset{S}{\|}}{P}OAg$$

$$(RO)_2\underset{\underset{S}{\|}}{P}OAg + HalR \rightarrow (RO)_2\underset{\underset{S}{\|}}{P}OR + AgHal \quad (I)$$

or II:



$$(RO)_2\underset{\underset{S}{\|}}{P}OM + AgNO_3 \rightarrow (RO)_2\underset{\underset{Ag-S-NO_3}{\|}}{P}OM \rightarrow$$

$$(RO)_2\underset{\underset{Ag-S-\boxed{NO_3}}{|}}{P}O\boxed{M} \rightarrow (RO)_2\underset{\underset{Ag-S}{|}}{P}=O \xrightarrow{+RHal} (RO)_2\underset{\underset{R-S}{|}}{P}=O \quad (II)$$

The preparation of phosphorothioic esters (I or II) could give some indication of the structure of silver dialkyl phosphorothioate, to which Pishchimuka [5] assigned the phosphorothiolate structure $(RO)_2\underset{\underset{O}{\|}}{P}-SAg$.

Phosphorothioic esters both of structure I and of structure II were prepared and described by Pishchimuka. It was thus possible by comparison of the properties of phosphorothioic esters prepared by us with those described by Pishchimuka to come to a conclusion regarding their structure. In all cases we obtained ester I, which has the phosphorothionate structure $(RO)_2\underset{\underset{S}{\|}}{P}OR$.

In order to study the effect of the metal of the salt on the double-decomposition reaction between metal dialkyl phosphorothioates and the corresponding alkyl halides, we have carried out reactions between sodium, potassium and silver diethyl phosphorothioates and ethyl bromide and iodide. The reactions were carried out either in a medium of dry ether or in absolute alcoholic solution. The results of the experiments are given in the table.

TABLE

No.	Reaction	Solvent	Result of reaction	B.p. (°C)	Pressure (mm Hg)	n_D^{22}	Yield (%)
1	$(C_2H_5O)_2\underset{\underset{S}{\|}}{P}ONa + C_2H_5Br$	Ether	Did not go	–	–	–	–
2	$(C_2H_5O)_2\underset{\underset{S}{\|}}{P}ONa + C_2H_5I$	Ether	$(C_2H_5O)_3P{=}S$	118	20	1.4520	2.9
3	$(C_2H_5O)_2\underset{\underset{S}{\|}}{P}ONa + C_2H_5I$	Alcohol	$(C_2H_5O)_3P{=}S$	114	17	1.4521	3.1
4	$(C_2H_5O)_2\underset{\underset{S}{\|}}{P}OK + C_2H_5Br$	Ether	Did not go	–	–	–	–
5	$(C_2H_5O)_2\underset{\underset{S}{\|}}{P}OK + C_2H_5Br$	Alcohol	$(C_2H_5O)_3P{=}S$	118	20	1.4520	55.8
6	$(C_2H_5O)_2\underset{\underset{S}{\|}}{P}OK + C_2H_5I$	Ether	$(C_2H_5O)_3P{=}S$	115	18	1.4523	4.2
7	$(C_2H_5O)_2\underset{\underset{S}{\|}}{P}OK + C_2H_5I$	Alcohol	$(C_2H_5O)_3P{=}S$	111	11	1.4520	41.5
8	$(C_2H_5O)_2\underset{\underset{S}{\|}}{P}OAg + C_2H_5I$	Ether	Did not go	–	–	–	–
9	$(C_2H_5O)_2\underset{\underset{S}{\|}}{P}OAg + C_2H_5I$	Alcohol	$(C_2H_5O)_3P{=}S$	110-111	11	1.4521	33.3

The product in these experiments was always the same triethyl phosphorothioate, but the yield was dependent on the nature of the metal of the salt. Thus, the potassium and silver salts gave higher yields of ester (55.8% and 33.3%) than the sodium salt (3%).

The yield of ester is undoubtedly affected by the nature of the halogen of the alkyl halide and also by the solubility of the salt in ether or alcohol. The ester-formation reaction goes better with ethyl iodide than with ethyl bromide. It was observed also that the formation of triethyl phosphorothioate does not go as well in ether as in alcohol. The formation of the same triethyl ester in all cases shows that sodium, potassium, and silver diethyl phosphorothioates all have the same structure.

EXPERIMENTAL

Action of Ethyl Iodide on Sodium Diethyl Phosphorothioate. Diethylphosphorous acid (25 g) was added dropwise to metallic sodium (4.1 g) in dry ether. With the first drops added, the formation of sodium diethylphosphite was evident. When addition of the acid was complete, the solution was heated until the sodium had disappeared (there was a 2.5-g excess of acid). When the solution was cool, a solution of sulfur (5 g) in benzene was added. The solution became yellow; it was boiled and left overnight. By the next day a white precipitate had settled on the bottom of the flask; the supernatent liquid was yellow. An ethereal solution of ethyl iodide (31.6 g) was added from a dropping funnel; no heating effect was observed. When the whole of the ethyl iodide had been added, the solution was heated at the boil for several hours. The precipitate at the bottom of the flask did not change in appearance; it was filtered off and washed with dry ether (37 g). The ether was distilled from the filtrate, and the residue was vacuum-distilled. At 118° under 20 mm pressure a substance (1 g, 2.9%) having n_D^{22} 1.4520 came over.

Action of Ethyl Iodide on Sodium Diethyl Phosphorothioate in Alcoholic Solution. An ethereal solution of ethyl iodide was added from a dropping funnel to a solution of sodium diethyl phosphorothioate (37 g) in absolute alcohol. There was no precipitate formed during addition of ethyl iodide. The solution was heated at the boil for three hours, and when it was cooled a small amount of white precipitate came down; it was filtered off. From the filtrate, ether and alcohol were driven off on a water bath. The residue was fractionated under reduced pressure, and a substance (1.2 g, 3.1%) of n_D^{22} 1.4521 came over at 114° under 17 mm pressure. Towards the end of the fractionation decomposition set in: white fumes appeared in the flask, and the voluminous white residue of unchanged sodium salt became distended.

Action of Ethyl Iodide on Potassium Diethyl Phosphorothioate. Metallic potassium (7 g) was introduced into dry ether contained in a round-bottomed flask provided with a reflux condenser, and an ethereal solution of diethylphosphorous acid (25 g) was added from a dropping funnel. With the first drops added white potassium diethylphosphite began to come down. When the whole of the acid had been added, the liquid was heated at the boil until the potassium had disappeared. When the solution was cool, a benzene solution of sulfur (5.79 g) was added, when the solution became yellow and a white precipitate formed on the bottom of the flask. The mixture was boiled for a long time: the white precipitate remained; the supernatent liquid was yellowish. A solution of ethyl iodide (28.2 g) in dry benzene was added to the cooled contents of the flask; there was no change in outward appearance, and no evolution of heat was to be observed. The mixture was heated at the boil for a considerable time. The residue, which had not changed in appearance, was filtered off and washed with dry ether (43 g). In the halogen test a faint flame coloration was obtained. The solvent was driven off the filtrate on a water bath, and the residue was fractionated under reduced pressure. The ester (1.5 g, 4.2%), which had n_D^{22} 1.4523, came over at 115-116° under 18 mm pressure. Towards the end of the fractionation decomposition set in.

Action of Ethyl Iodide on Potassium Diethyl Phosphorothioate in Alcoholic Solution. The 43 g of potassium salt isolated in the preceding experiment was dissolved in absolute alcohol, and to the solution obtained the ethyl iodide driven off in the course of the previous experiment was added. When the addition was almost complete, a white precipitate came down. The mixture was heated at the boil for four hours, and the amount of precipitate increased. The flask was allowed to stand overnight, and on the next day the precipitate was filtered off and washed with dry ether: 14.5 g of potassium iodide was obtained (test for halogen). When the solvent was driven from the filtrate, more potassium iodide was precipitated, and the total yield of potassium iodide was 19 g (55.4%). Addition of dry ether to the residual solution produced a white precipitate of unchanged potassium diethyl phosphorothioate (3.2 g); it gave a negative test for halogen. The residue, after removal of solvent on the water bath, was vacuum-fractionated, yielding 17 g (35.2%) of a substance of b.p. 111° at 11 mm and n_D^{22} 1.4520.

Action of Ethyl Bromide on Potassium Diethyl Phosphorothioate, in Alcoholic Solution. An excess of ethyl bromide was added to a solution of potassium diethyl phosphorothioate (3.2 g) in absolute alcohol. A white precipitate formed, and when the mixture was boiled the amount of precipitate increased; boiling was continued for four hours, and the mixture was then cooled. The precipitate (KBr: the test for halogen was positive) was filtered off. Alcohol was distilled off the filtrate, and the residue was vacuum-fractionated, yielding a substance (1.7 g, 55.8%) of b.p. 118°/20 mm and n_D^{22} 1.4520.

Action of Ethyl Iodide on Silver Diethyl Phosphorothioate. The silver salt (4.5 g) was added to dry ether contained in a round-bottomed flask fitted with a reflux condenser, and ethyl iodide (2.5 g) was added from a dropping funnel: there was no change in outward appearance. The mixture was boiled for two hours, and the salt still did not change in appearance (the reaction had not gone). Absolute alcohol was added until the silver salt had dissolved completely, and the resulting brownish solution was heated to the boil. The whole picture changed: the solution became colorless, and a yellowish precipitate of silver iodide began to appear and continued to increase in volume as boiling continued. The mixture was cooled, and the precipitate was filtered off and washed with dry ether (3.0 g, 78.9%). Alcohol was distilled from the filtrate, and the residue was vacuum-fractionated, yielding 1 g (33.3%) of ester of b.p. 111°/14 mm and n_D^{22} 1.4520. The high yield of potassium iodide indicates that the reaction went very well, but owing to the small quantities concerned, it was difficult to make an accurate estimate of the amount of ester formed.

SUMMARY

1. The yield in the reaction leading to the formation of triethyl phosphorothioate depends on the nature of the metal in the metal dialkyl phosphorothioate, on the nature of the halogen in the alkyl halide, and on the conditions of the experiment:

a) silver and potassium diethyl phosphorothioates give the highest yields of ester;
b) the highest yields of ester are obtained in alcoholic solution.

2. In the reaction of ethyl iodide and bromide with sodium, potassium, and silver diethyl phosphorothioates the same triethyl phosphorothioate is obtained in varying yield.

LITERATURE CITED

[1] A. E. Arbuzov, "The Structure of Phosphorous Acid and its Derivatives", St. Petersburg, 1905 (Dissertation).

[2] A. E. Arbuzov and O. M. Shanshinskaya, Trans. Kazan. Chem. Tech. Inst., 16 (1949).

[3] A. E. Arbuzov, J. Russ. Phys.-Chem. Soc., 61, 231 (1929).

[4] A. E. Arbuzov et al, J. Gen. Chem., 2, 345 (1932).

[5] P. S. Pishchimuka, J. Russ. Phys.-Chem. Soc., 44, 1406 (1912).

Received June 23, 1952

S. M. Kirov Kazan Chemical and Tecnological Institute

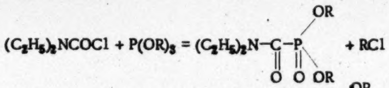
N,N-DIETHYL(DIALKOXYPHOSPHINYL)FORMAMIDES

B. A. Arbuzov and N. I. Rizpolozhensky

A. E. Arbuzov and Dunin [1] prepared ethyl diethoxyphosphinylformate by the action of chloroformic ester on triethyl phosphite, and they studied some of its properties. Nylen [2] prepared diethoxyphosphinylformamide (diethyl carbamoylphosphonate) by the action of aqueous ammonia on this ester. In 1924, Nylen [3] attempted to prepare esters of acylphosphonic (α-keto phosphonic) acids by the action of acid anhydrides on sodium diethyl phosphite. However, it was found that the reaction went in an abnormal fashion, and the expected acylphosphonic acids were not obtained. Kabachnik and Rossiiskaya [4] showed that acylphosphonic esters were obtained by the action of acid anhydrides on full esters of phosphorous acid in accordance with the A.E. Arbuzov scheme. A. E. Arbuzov and Azanovskaya [5] elucidated the source of Nylen's lack of success in his attempts to synthesize acylphosphonic esters by the action of acid anhydrides on sodium diethyl phosphite: they found that sodium diethyl phosphite may add at the carbonyl group of acylphosphonic esters.

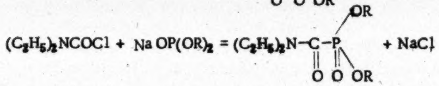
In this paper the preparation and properties of N,N-diethyl(dialkoxyphosphinyl)formamides are described. We prepared them by the action of diethylcarbamoyl chloride both on full esters of phosphorous acid, and also on sodium dialkyl phosphites:

1)



$$(C_2H_5)_2NCOCl + P(OR)_3 = (C_2H_5)_2N-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{P}(OR)_2 + RCl$$

2)



$$(C_2H_5)_2NCOCl + NaOP(OR)_2 = (C_2H_5)_2N-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{P}(OR)_2 + NaCl$$

The two methods give approximately equal yields of N,N-diethyl(dialkoxyphosphinyl)formamides. We have prepared a number of these compounds, and their physical properties are given in the table.

We were not successful in preparing the dimethoxy compound in a pure form by either method.

EXPERIMENTAL

Attempt to Synthesize N,N-Diethyl(dimethoxyphosphinyl)formamide

Trimethyl phosphite (9.7 g) was introduced into a three-necked flask provided with reflux condenser and thermometer, and diethylcarbamoyl chloride (10.7 g) was added. There was no reaction at room temperature, and the flask was placed on the bath. At 122-125° (thermometer in the flask) methyl chloride began to be evolved. The temperature in the flask was raised gradually (over 25-30 minutes) to 135°, and was maintained at that level for 90 minutes. Evolution of methyl chloride ceased. The contents of the flask – a clear, yellowish liquid – were vacuum-distilled from an Arbuzov flask and yielded the following fractions:

Fr. I, b.p. 30- 85° at 10-11 mm	1.5 g
Fr. II, b.p. 70-118° at 4 mm	
Fr. III, b.p. 119-130° at 4 mm;	4 g

the residue in the flask (3 g) was a syrupy liquid.

Four vacuum fractionations were carried out without succeeding in isolating any N,N-diethyl(dimethoxyphosphinyl)formamide. Attempts to prepare this compound via sodium dimethyl phosphite were unsuccessful also.

Synthesis of N,N-Diethyl(diethoxyphosphinyl)formamide

a) A mixture of triethyl phosphite (10 g) and diethylcarbamoyl chloride (8.2 g) was heated on a bath

TABLE

No.	Formula	B.p. (°C)	Pressure (mm Hg)	d_4^{25}	n_D^{25}	MR_D	
						Found	Calc'd
1	$(C_2H_5)_2N\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{P}(OC_2H_5)_2$	117-119	4	1.0806	1.4470	58.67	58.23
2	$(C_2H_5)_2N\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{P}(OC_3H_7\text{-n})_2$	131-132	2	1.0453	1.4478	67.91	67.44
3	$(C_2H_5)_2N\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{P}(OC_3H_7\text{-i})_2$	114-115	1.5	1.0339	1.4430	68.01	67.44
4	$(C_2H_5)_2N\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{P}(OC_4H_9\text{-n})_2$	148.5-149.5	5	1.0202	1.4480	76.98	76.70
5	$(C_2H_5)_2N\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{P}(OC_5H_{11}\text{-i})_2$	155-155.5	4	0.9963	1.4482	86.54	85.95
6	$(C_2H_5)_2N\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{P}(OC_6H_{13}\text{-n})_2$	183-184.5	3.5	0.9709	1.4458	95.91	95.17

in a three-necked flask provided with reflux condenser and thermometer. At 140-145° ethyl chloride began to be evolved in appreciable amount. The reaction flask was maintained at 145-150° (thermometer in the flask) for two hours, and the temperature was then raised to 165° for 30 minutes. Separation of ethyl chloride ceased. By vacuum distillation from an Arbuzov flask the following fractions were obtained:

Fr. I, b.p. to 65° at 4 mm; 1.6 g
Fr. II, b.p. 65-115° at 4 mm; 1.2 g
Fr. III, b.p. 115-120° at 4 mm; 9 g

The residue (1 g) in the flask was a viscous yellow syrup. A second fractionation of the fraction of b.p. 115-120°/4 mm gave:

Fr. I, b.p. to 117° at 4 mm; 1.1 g
Fr. II, b.p. 117-119 at 4 mm; 7 g.

The product (7 g, 49%) had the following constants: b.p. 117-119° at 4 mm; n_D^{25} 1.4470; d_4^{25} 1.0806; yi [illegible]

Found MR_D 58.67
$C_9H_{20}O_4PN$. Calculated MR_D 58.23

Found %: P 13.20; 13.27
$C_9H_{20}O_4PN$. Calculated %: P 13.12

N,N-Diethyl(diethoxyphosphinyl)formamide is a colorless odorless liquid, soluble in organic solvents such as ether, benzene, and gasoline.

b) Sodium (5 g) and gasoline of b.p. 80-120° (150 ml) were introduced into a three-necked flask provided with stirrer, reflux condenser, and dropping funnel.

Diethylphosphorous acid (21.2 g) was added from the dropping funnel, and the flask was heated for one hour on the water bath. The excess of sodium was removed, and to the cooled solution of sodium diethyl phosphite diethylcarbamoyl chloride (20.8 g) was added dropwise. Reaction was accompanied by evolution of heat. When the whole (the calculated amount) of the diethylcarbamoyl chloride had been added, the flask was heated on the water bath for 90 minutes. The precipitate of sodium chloride was separated by centrifuging, , and the residual liquid after removal of the gasoline was vacuum-fractionated from an Arbuzov flask. The following fractions were isolated:

Fr. I, b.p. to 60° at 12 mm; 4 g
Fr. II, b.p. 50-109° at 3 mm; 1.8 g
Fr. III, b.p. 109-120° at 3 mm } 29.2 g
Fr. IV, b.p. 120-125° at 3 mm }

Fractions III and IV were refractionated:

Fr. I, b.p. to 120° at 6 mm } 3 g
Fr. II, b.p. 120-122° at 6 mm }
Fr. III, b.p. 122-123° at 6 mm; 24 g

The residue weighed 0.5 g.

The product (24 g, 65.8%) had b.p. 122-123° at 6 mm; d_4^{25} 1.0808; n_D^{25} 1.4475; yi

Found %: P 13.19; 13.18
$C_9H_{20}O_4PN$. Calculated %: P 13.12

Synthesis of N,N-Diethyl(diisopropoxyphosphinyl)formamide

a) Triisopropyl phosphite (10.4 g) and diethylcarbamoyl chloride (6.7 g) were introduced into an Arbuzov flask. The flask was heated on an oil bath, and at 165-168° (thermometer in liquid) reaction set in with evolution of isopropyl chloride. The temperature of the bath was gradually raised over a period of 40 minutes to 185°, and separation of isopropyl chloride ceased; 3.2 g was driven over (theory requires 3.92 g). The reaction product – an almost colorless liquid – was vacuum-fractionated, yielding the following fractions:

Fr. I, b.p. to 114° at 3 mm; 1.5 g
Fr. II, b.p. 114-120° at 3 mm; 11 g.

The residue in the flask weighed 0.6 g.

Further fractionation of the fraction of b.p. 114-120°/3 mm yielded:

Fr. I, b.p. to 113° at 1 mm; 2.5 g
Fr. II, b.p. 113-114° at 1 mm; 7 g
Fr. III, b.p. 114-118° at 1 mm; 0.8 g

The product (7 g, 53.7%) – a colorless, odorless liquid – has the following constants: b.p. 113-114° at 1 mm; d_4^{25} 1.0335; n_D^{25} 1.4478; yiel

Found %: P 11.83, 11.68
$C_{11}H_{24}O_4PN$. Calculated %: P 11.71

b) Sodium diisopropyl phosphite was prepared in a three-necked flask provided with stirrer, dropping funnel, and reflux condenser by the action of sodium (4 g, an excess) on diisopropylphosphorous acid (11.9 g). Gasoline of b.p. 80-120° served as solvent. Diethylcarbamoyl chloride (10 g) was added over 20 minutes from the dropping funnel to the sodium diisopropyl phosphite, and reaction set in with evolution of heat. When the addition was complete, the contents of the flask were boiled for 90 minutes. The precipitate of sodium chloride was removed by centrifuging, and the residue after removal of the gasoline was vacuum-fractionated from an Arbuzov flask. The following fractions were obtained:

Fr. I, b.p. to 115° at 3 mm; 2.7 g
Fr. II, b.p. 115-119° at 3 mm; 2.8 g
Fr. III, b.p. 119-120° at 3 mm; 9.4 g

The residue in the flask weighed 0.5 g.

Further fractionation of Fractions II and III yielded:

Fr. I, b.p. to 114° at 1.5 mm; 1.5 g
Fr. II, b.p. 114-115° at 1.5 mm; 10 g
Fr. III, b.p. 115.5-118° at 1.5 mm; 2 g

The product (10 g, 51.5%) had the following constants: b.p. 114-115° at 1.5 mm; d_4^{25} 1.0339; n_D^{25} 1.4430;

Found MR_D 68.01
$C_{11}H_{24}O_4PN$. Calculated MR_D 67.44

Found %: P 11.88; 11.78
$C_{11}H_{24}O_4PN$. Calculated %: P 11.71

Synthesis of N,N-Diethyl(dipropoxyphosphinyl)formamide

Sodium dipropyl phosphite was prepared in a three-necked flask provided with stirrer, reflux condenser, and dropping funnel from dipropylphosphorous acid (8.7 g) and sodium (4 g, an excess). Gasoline of b.p. 80-120°

was employed as solvent. Diethylcarbamoyl chloride (7 g) was added from the dropping funnel to the solution of sodium dipropyl phosphite, and reaction set in with evolution of heat. When the whole (the calculated amount) of the acid chloride had been added, the contents of the flask were boiled for 90 minutes. Sodium chloride, which was formed in a colloidal condition, came down as a precipitate after an addition of water (4-5 drops), and it was filtered off under suction. The residue after removal of gasoline was vacuum-fractionated from an Arbuzov flask, yielding:

Fr. I, b.p. to 130° at 2 mm; 1.8 g
Fr. II, b.p. 130-134° at 2 mm; 10.5 g

The residue weighed 0.6 g.

Further fractionation of the fraction of b.p. 130-134°/2 mm gave:

Fr. I, b.p. to 131° at 2 mm; 0.5 g
Fr. II, b.p. 131-132° at 2 mm; 7.5 g
Fr. III, b.p. 132-136° at 2 mm; 0.3 g

The product (7.5 g, 54.8%) – a colorless odorless liquid – had the following constants: b.p. 131-132° at 2 mm; d_4^{25} 1.0453; n_D^{25} 1.4478; [illegible]

Found MR_D 67.91
$C_{11}H_{24}O_4PN$. Calculated MR_D 67.44

Found %: P 11.63; 11.6
$C_{11}H_{24}O_4PN$. Calculated %: P 11.71

Preparation of N,N-Diethyl(dibutoxyphosphinyl)formamide

a) Diethylcarbamoyl chloride (6.5 g) and tributyl phosphite (12 g) were introduced into an Arbuzov flask, which was heated on an oil bath. Reaction set in at 170°, butyl chloride being driven off. The temperature of the bath was raised slowly over one hour to 185°, and butyl chloride ceased to come over (4 g was driven over). The reaction product was vacuum-fractionated and yielded:

Fr. I, b.p. to 140° at 5 mm; 2.7 g
Fr. II, b.p. 140-150° at 5 mm; 9.3 g

The residue in the flask weighed 1.4 g.

Further fractionation of the fraction of b.p. 140-150° yielded:

Fr. I, b.p. to 148° at 5 mm; 1.5 g
Fr. II, b.p. 148.5-149.5 at 5 mm; 7.2 g

The product (7.2 g, 51.4%) – a colorless odorless liquid – had the following constants: b.p. 148.5-149.5° at 5 mm; d_4^{25} 1.0202; n_D^{25} 1.4480; [illegible]

Found MR_D 76.98
$C_{13}H_{28}O_4PN$. Calculated MR_D 76.70

Found %: P 10.72; 10.68
$C_{13}H_{28}O_4PN$. Calculated %: P 10.57

b) Sodium dibutyl phosphite was prepared in a three-necked flask by the method described above from dibutylphosphorous acid (11.5 g) and sodium (4 g); the solvent was gasoline of b.p. 80-120°. Diethylcarbamoyl chloride (8.1 g) was added slowly to the solution of sodium dibutyl phosphite, and reaction set in with evolution of heat. When all the acid chloride had been added, the mixture was boiled on the water bath for two hours. The sodium chloride formed, which was in a colloidal condition, came out in finely crystalline form on addition of water (0.5 ml); it was filtered off under suction. The benzene was driven off under reduced pressure, and the residue was vacuum-fractionated from an Arbuzov flask, yielding:

Fr. I, b.p. to 148° at 5 mm; 2 g
$\left.\begin{array}{l}\text{Fr. II, b.p. 148-150° at 5 mm}\\ \text{Fr. III, b.p. 150-151° at 5 mm}\end{array}\right\}$ 10.5 g

A further fractionation of fractions II and III yielded:

Fr. I, b.p. to 148.5° at 5 mm; 0.7 g
Fr. II, b.p. 149-150° at 5 mm; 9.4 g

The product (9.4 g, 53.7%) had the following constants: b.p. 149-150° at 5 mm; d_4^{25} 1.0205; n_D^{25} 1.4474;

Preparation of N,N-Diethyl(diisopentyloxyphosphinyl)formamide

Sodium diisopentyl phosphite was prepared by the method described above in a gasoline medium from diisopentylphosphorous acid (8.7 g) and sodium (4 g). Diethylcarbamoyl chloride (5.3 g) was added dropwise to the solution of sodium dissopentyl phosphite, and reaction set in with evolution of heat. The flask was then heated on the water bath for two hours. Sodium chloride formed in the colloidal state and was precipitated in a finely crystalline condition by addition of water (0.5 ml). The precipitate of sodium chloride was filtered off under suction, and gasoline was removed under reduced pressure. The residue was vacuum-fractionated from an Arbuzov flask:

Fr. I, b.p. to 150° at 5 mm; 2 g
Fr. II, b.p. 150-162° at 5 mm; 9 g

A further fractionation of Fraction II yielded:

Fr. I, b.p. to 155° at 4 mm; 0.5 g
Fr. II, b.p. 155-155.5° at 4 mm; 6.5 g
Fr. III, b.p. 156-160° at 4 mm; 0.4 g

The product (6.5 g, 51.8%) – a colorless, odorless liquid – had the following constants: b.p. 155-155.5° at 4 mm; d_4^{25} 0.9963; n_D^{25} 1.4482;

Found MR_D 86.54
$C_{15}H_{32}O_4PN$. Calculated MR_D 85.95

Found %: P 9.79; 9.64
$C_{15}H_{32}O_4PN$. Calculated %: P 9.66

Preparation of N,N-Diethyl(dihexyloxyphosphinyl)formamide

Sodium dihexyl phosphite was prepared in a gasoline medium from dihexylphosphorous acid (10.5 g) and sodium (4 g) by the method already described. Diethylcarbamoyl chloride (4.4 g) was added dropwise to the solution of sodium dihexyl phosphite, and reaction set in with evolution of heat. The mixture was boiled on the water bath for two hours. Sodium chloride formed in the colloidal state and was precipitated in a crystalline condition by addition of water (0.5 ml). The precipitate of sodium chloride was filtered off under suction. The residue after removal of gasoline was vacuum-fractionated from an Arbuzov flask, yielding:

Fr. I, b.p. to 168° at 2.5 mm; 1.4 g
Fr. II, b.p. 168-186° at 2.5 mm; 7.2 g

Further fractionation of Fraction II gave:

Fr. I; b.p. to 170° at 3.5 mm; 0.9 g
Fr. II, b.p. 170-183° at 3.5 mm; 0.7 g
Fr. III, b.p. 183-184.5° at 3.5 mm; 4.8 g

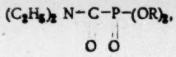
The product (4.8 g, 43%) – a colorless, odorless liquid – had the following constants: b.p. 183-184.5° at 3.5 mm; d_4^{25} 0.9709; n_D^{25} 1.4458;

Found MR_D 95.91
$C_{17}H_{36}O_4PN$. Calculated MR_D 95.17

Found %: P 8.96; 8.82
$C_{17}H_{36}O_4PN$. Calculated %: P 8.88

SUMMARY

By the action of diethylcarbamoyl chloride on trialkyl phosphite or on sodium dialkyl phosphite, the following new N,N-diethyl(dialkoxyphosphinyl)formamides have been prepared:



$$(C_2H_5)_2N-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{P}-(OR)_2$$, where R = C_2H_5; n-C_3H_7; i-C_3H_7;

n-C_4H_9; i-C_5H_{11}, and n-C_6H_{13}.

LITERATURE CITED

[1] A. E. Arbuzov and A. A. Dunin, J. Russ. Chem. Soc., 46, 295 (1914).

[2] P. Nylen , Ber. 57, 1023 (1924); 59, 1119 (1926).

[3] P. Nylen, Ber. 57, 1023 (1924).

[4] M.I. Kabachnik and P. A. Rossiiskaya, Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci., No. 4, 364 (1945).

[5] A.E. Arbuzov and M.M. Azanovskaya, Proc. Acad. Sci. U.S.S.R., 58, 9, 1961 (1947).

Received June 23, 1952

A. E. Arbuzov Chemical Institute of
the Kazan Affiliated Institute
of the U.S.S.R. Academy of Sciences

ESTERS OF ETHYLPHOSPHONOUS ACID, AND SOME OF THEIR REACTIONS

COMMUNICATION I. FULL ESTERS OF ETHYLPHOSPHONOUS ACID

B. A. Arbuzov and N. I. Rizpolozhensky

Whereas arylphosphonous esters have received fairly detailed study [1], alkylphosphonous esters have scarcely been described. Kamai [2] has described a number of diphenyl alkylphosphonites, which he prepared by the action of diphenyl phosphorochloridite on the corresponding alkylmagnesium bromides. The cause of the lack of attention given to alkylphosphonous esters lies, evidently, in the poor accessibility of alkylphosphonous dichlorides, the starting materials for the preparation of alkylphosphonous esters.

In 1949 Kharasch [4] worked out a convenient, accessible method for the preparation of ethylphosphonous dichloride by the action of phosphorus trichloride on tetraethyl-lead, and in 1950 Fox [3] synthesized a number of alkylphosphonous dichlorides by the action of organocadmium compounds on phosphorus trichloride. From A. E. Arbuzov's work [1] it is known that arylphosphonous esters are very reactive, and this gave grounds for supposing that ethylphosphonous esters would be still more reactive.

In the present communication results are given relating to the synthesis and certain properties of esters of ethylphosphonous acid. The esters were prepared by the action of the corresponding alcohols on ethylphosphonous dichloride in presence of pyridine or triethylamine:

$$C_2H_5PCl_2 + 2ROH + 2C_5H_5N = C_2H_5P(OR)_2 + 2C_5H_5N \cdot HCl.$$

Properties of esters prepared in this way are given in Table 1.

TABLE 1

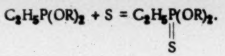
No.	Formula	B.p. (°C)	Pressure (mm Hg)	d_4^{20}	n_D^{20}	MR_D Found	MR_D Calc'd·	Yield (%)
1	$C_2H_5P(OCH_3)_2$	73.5-74.5	225	0.9516	1.4210	32.53	32.14	35.0
2	$C_2H_5P(OC_2H_5)_2$	58-60	38	0.9207	1.4212	41.34	41.39	64.5
3	$C_2H_5P(OC_3H_7\text{-}n)_2$	65-66.5	11	0.9021	1.4278	50.78	50.62	63.7
4	$C_2H_5P(OC_3H_7\text{-}i)_2$	73.5-74.5	35	0.8844	1.4169	50.64	50.62	40.0
5	$C_2H_5P(OC_4H_9\text{-}n)_2$	63-64	3	0.8977	1.4353	59.96	59.86	80.0
6	$C_2H_5P(OC_6H_{13}\text{-}n)_2$	100-101	2	0.8875	1.4435	78.41	78.33	92.0
7	$C_2H_5P(OC_8H_{17}\text{-}n)_2$	142-144	3	0.8809	1.4439	96.89	96.8	90.0
8	$C_2H_5P(OC_6H_5)_2$	115-115.5	1	1.1030	1.5650	72.57	71.13	72.5

Kamai [2] cites constants for diphenyl ethylphosphonite that differ greatly from our values: B.p. 223-225° at 11 mm; d_0^{16} 1.1923; d_D^{16} 1.5912.

Ethylphosphonous esters are colorless liquids of characteristic unpleasant odor. The odors of the methyl and the ethyl esters are very similar to those of trimethyl and triethyl phosphite respectively. They all readily oxidize in the air, oxidation being particularly vigorous in the case of the methyl and ethyl esters, which burst into flame when poured on filter paper. Hence, all operations with the esters were carried out in an atmosphere of carbon dioxide.

As was to be expected, ethylphosphonous esters were found to be extremely reactive. Being tervalent phosphorus derivatives, they react with cuprous iodide: the compound with the dimethyl ester, $C_2H_5P(OCH_3)_2 \cdot CuI$, has m.p. 160-161°; that formed with the diethyl ester, $C_2H_5P(OC_2H_5)_2 \cdot CuI$, has m.p. 167-168°. The complex compounds with the dipropyl ester, $C_2H_5P(OC_3H_7\text{-}n)_2 \cdot CuI$, and the diphenyl ester, $C_2H_5P(OC_6H_5)_2 \cdot CuI$, are noncrystallizing sirups.

Ethylphosphonous esters undergo a vigorous addition reaction with sulfur with formation of ethylphosphonothionic esters:



$$C_2H_5P(OR)_2 + S = C_2H_5\underset{\underset{S}{\|}}{P}(OR)_2.$$

The properties of the esters prepared in this way are given in Table 2.

Addition of sulfur occurs also with ethylphosphonous dichloride. As is known, this reaction has been carried out by heating ethylphosphonous dichloride with sulfur in sealed tubes [5].

We have found that in presence of a small amount of aluminum chloride the addition reaction takes place at room temperature with great vigor and with evolution of much heat. Thus, addition of 0.1 g of aluminum chloride to a mixture of ethylphosphonous dichloride (6.2 g) and sulfur (1.5 g) causes the temperature to rise to 154°.

TABLE 2

No.	Formula	B.p. (°C)	Pressure (mm Hg)	d_4^{20}	n_D^{20}	MR_D Found	MR_D Calc'd.	Yield (%)
1	$C_2H_5\underset{\underset{S}{\|}}{P}(OC_2H_5)_2$	80.5-81	10	1.0356	1.4558	47.84	47.82	74.0
2	$C_2H_5\underset{\underset{S}{\|}}{P}(OC_3H_7\text{-}n)_2$	69-70	1.5	1.0005	1.4622	57.08	57.80	56.5
3	$C_2H_5\underset{\underset{S}{\|}}{P}(OC_6H_5)_2$	144-144.5	1	1.1811	1.5772	77.58	78.08	65.8
4	$C_2H_5\underset{\underset{S}{\|}}{P}Cl_2$	88.5-89	46	1.3550	1.5440	36.56	37.97	71.0

The ethylphosphonothionic esters that we prepared are fuming liquids of characteristic odor.

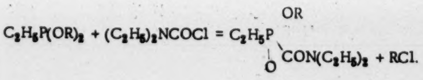
By the action of halogen derivatives of hydrocarbons, ethylphosphonous esters readily undergo the A. E. Arbuzov rearrangement. To exemplify this we have carried out the following reactions: reaction of the diethyl ester with ethyl iodide and with butyl bromide, reaction of the dipropyl ester with propyl iodide, reaction of the dimethyl, diethyl, and dipropyl esters with carbon tetrachloride (Kamay [6]), and reaction of the ethyl and propyl esters with ethyl chloroacetate (A.E. Arbuzov and Dunin [7]).

Constants of the compound are given in Table 3.

TABLE 3

No.	Formula	B.p.(°C)	Pressure (mm Hg)	d_4^{20}	n_D^{20}	MR_D Found	MR_D Cal'd.	Yield %
1	$(C_2H_5)_2\underset{\underset{O}{\|}}{P}OC_2H_5$	87-88	12	0.9983	1.4353	39.27	39.13	77.0
2	$C_2H_5\underset{\underset{O}{\|}}{P}(n\text{-}C_4H_9)(OC_2H_5)$	106-108	10	0.9939	1.4382	47.09	48.36	25.7
3	$C_2H_5\underset{\underset{O}{\|}}{P}(OC_3H_7\text{-}n)(n\text{-}C_3H_7)$	104-105	8	0.9657	1.4370	48.35	48.37	30.0
4	$C_2H_5\underset{\underset{O}{\|}}{P}(CCl_3)(OCH_3)$	80-81	2.5	1.4174	1.4889	45.92	44.50	21.4
5	$C_2H_5\underset{\underset{O}{\vert}}{P}(CCl_3)(OC_2H_5)$	83-84	1.5	1.3476	1.4819	50.66	49.11	22.1
6	$C_2H_5\underset{\underset{O}{\vert}}{P}(CCl_3)(OC_3H_7\text{-}n)$	88-89	1.5	1.2790	1.4674	55.03	53.73	35.0
7	$C_2H_5\underset{O}{P}\begin{matrix}OC_2H_5\\CH_2COOC_2H_5\end{matrix}$	96-96.5	1	1.0935	1.4443	50.84	50.02	65.0
8	$C_2H_5\underset{O}{P}\begin{matrix}OC_3H_7\text{-}n\\CH_2COOC_2H_5\end{matrix}$	104-105	1	1.0649	1.4420	55.45	54.64	56.0

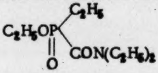
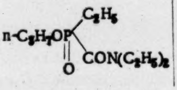
Diethylcarbamoyl chloride will react with ethylphosphonous ester, yielding the diethylamide of an alkoxy(ethyl)phosphinylformic acid according to the equation:



$$C_2H_5P(OR)_2 + (C_2H_5)_2NCOCl = C_2H_5\underset{O}{P}\begin{matrix}OR\\CON(C_2H_5)_2\end{matrix} + RCl.$$

Properties of the compounds obtained are given in Table 4.

TABLE 4

No.	Formula	B.p. (°C)	Pressure (mm Hg)	d_4^{20}	n_D^{20}	MR_D		Yield (%)
						Found	Cal'd.	
1	 $C_2H_5OP(=O)(C_2H_5)CON(C_2H_5)_2$	106-107	1.5	1.0535	1.4625	57.69	56.59	53.5
2	 $n\text{-}C_3H_7OP(=O)(C_2H_5)CON(C_2H_5)_2$	109-110	1	1.0341	1.4597	62.20	61.21	45.6

EXPERIMENTAL

Preparation of Ethylphosphonous Esters

1. Dimethyl ethylphosphonite. Methanol (11.9 g), triethylamine (40.5 g: an excess of 2.5 g), and ether (200 ml) were introduced into a three-necked flask provided with stirrer, reflux condenser, and dropping funnel. Ethylphosphonous dichloride of b.p. 112-114° (24.5 g) was added dropwise with snow cooling and vigorous stirring, and a stream of dry carbon dioxide was passed throughout the reaction. When the whole of the acid chloride had been added, stirring was continued for a further one hour. Triethylamine hydrochloride was filtered off, and the filtrate, after removal of ether, was vacuum-distilled. A fraction of b.p. 35-80°/213 mm was obtained, and this, after two redistillations, yielded a fraction (8 g, 30%) of b.p. 73.5-74.5°/225 mm.

Dimethyl ethylphosphonite is a colorless mobile liquid having an odor similar to that of trimethyl phosphite. It burst into flame in air, and therefore all operations from the time of its preparation to that at which the constants were determined were carried out in a carbon dioxide atmosphere. The constants found for the ester were: d_4^{20} 0.9515; n_D^{20} 1.4210; found MR_D 32.53; calculated $C_4H_{11}O_2P$ MR_D 32.14.

Analysis of ethylphosphonous esters for phosphorus by the usual methods did not give reproducible results, owing to the ready oxidizability of these substances. We carried out the analysis as follows: The weighed amount of the substance was introduced into an ampoule having very thin walls, and the capillary of the ampoule was sealed. The ampoule was placed in a thick-walled Carius tube, into which a mixture of nitric acid (2 ml; sp. gr. 1.5) and sulfuric acid (8-10 ml; sp. gr. 1.84) was poured. The tube was sealed and cooled. The tube was then shaken vigorously in order to break the ampoule, and was then heated in a furnace at 250-300° for 10-12 hours. The further course of the analysis was by Neuman's method. Very good results were obtained by the use of this modified method.

Found %: P 25.02; 24.98
$C_4H_{11}O_2P$. Calculated %: P 25.35

2. Diethyl ethylphosphonite. In the preparation of this and all succeeding esters of ethylphosphonous acid, all operations were carried out in a carbon dioxide atmosphere. Starting with ethanol (17.7 g), ethylphosphonous dichloride (25.2 g), and pyridine, (31.2 g) in a medium of ether, we obtained, after the operations described for the preparation of the dimethyl ester, diethyl ethylphosphonite (20 g, 64.3%) having the following constants: B.p. 58-60° at 38 mm; d_4^{20} 0.9275; n_D^{20} 1.4212; found MR_D 41.34; calculated $C_6H_{15}O_2P$ MR_D 41.31.

Found %: P 20.52; 20.35
$C_6H_{15}O_2P$. Calculated %: P 20.65

The ester is a colorless liquid that smells like triethyl phosphite. When poured on filter paper, it takes fire and gives forth a large amount of smoke.

3. Dipropyl ethylphosphonite. The starting materials were: propyl alcohol (30.1 g), pyridine (43 g), and ethylphosphonous dichloride (33 g). The following fractions were obtained:

Fr. I	B.p. 35 - 60° at 11 mm;	4.1 g
Fr. II	B.p. 60 - 65° at 11 mm;	1.2 g
Fr. III	B.p. 65 - 75° at 11 mm;	34 g

Residue: 3.8 g

Further fractionation of Fractions II and III yielded dipropyl ethylphosphonite (28 g, 63.7%) having the following constants: B.p. 65-66 at 11 mm; d_4^{20}, 0.9021; n_D^{20} 1.4278; found MR_D 50.78; calculated $C_8H_{19}O_2P$ MR_D 50.62.

Found %: P 17.37; 17.36
$C_8H_{19}O_2P$. Calculated %: P 17.40

4. Diisopropyl ethylphosphonite. The starting materials were: isopropyl alcohol (20.5 g), triethylamine (30.6 g), and ethylphosphonous dichloride (22 g) in a medium of ether. Fractionation of the reaction product yielded:

Fr. I, B.p. 35 - 62° at 45 mm; 2.5 g
Fr. II, B.p. 62 - 77° at 45 mm; 2.1 g
Fr. III, B.p. 74 - 83° at 35 mm; 20.0 g

Residue: 3 g

Further fractionation of Fractions II and III yielded diisopropyl ethylphosphonite (11 g, 36%) having the following constants: B.p. 73.5-74.0° at 35 mm; d_4^{20} 0.8844; n_D^{20} 1.4169; found MR_D 50.64; calculated $C_8H_{19}O_2P$ MR_D 50.62.

Found %: P 17.58; 17.45
$C_8H_{19}O_2P$. Calculated %: P 17.40

5. Dibutyl ethylphosphonite. Starting with butyl alcohol (39.7 g), pyridine (45 g), and ethylphosphonous dichloride (35.1 g) in an ether medium, we obtained the following fractions:

Fr. I, B.p. 35 - 63° at 3 mm; 4 g
Fr. II, B.p. 63 - 80° at 3 mm; 48 g

Residue: 4.5 g

Refractionation of Fraction II yielded dibutyl ethylphosphonite (44 g, 79.4%) having the following constants: B.p. 63-63.5° at 3 mm; d_4^{20} 0.8977; n_D^{20} 1.4353; found MR_D 59.96; calculated $C_9H_{21}O_2P$ MR_D 59.86.

Found %: P 15.20; 15.16
$C_9H_{21}O_2P$. Calculated %: P 15.04

The ester is a liquid, of characteristic odor, nonwetting to glass.

6. Dihexyl ethylphosphonite. Starting with hexyl alcohol (36.2 g), pyridine (30 g), and ethylphosphonous dichloride (23.2 g) in an ether medium, we obtained the following fractions:

Fr. I, B.p. 35 - 99° at 2 mm; 0.5 g
Fr. II, B.p. 99 -102° at 2 mm; 44.5 g

Residue: 0.3 g

Refractionation yielded dihexyl ethylphosphonite (43 g, 92%) having the following constants: B.p. 100-101° at 2 mm; d_4^{20} 0.8875; n_D^{20} 1.4435; found MR_D 78.41; calculated $C_{14}H_{31}O_2P$ MR_D 78.33.

Found %: P 11.78; 11.69
$C_{14}H_{31}O_2P$. Calculated %: P 11.82

The ester is a liquid, nonwetting to glass.

7. Dioctyl ethylphosphonite. Starting with octyl alcohol (32 g), triethylamine (25 g), and ethylphosphonous dichloride (15 g), we obtained the following fractions:

Fr. I, B.p. 70 - 138° at 3 mm; 2.1 g
Fr. II, B.p. 138 - 146° at 3 mm; 31 g

Residue: 3 g

Refractionation of Fraction II yielded dioctyl ethylphosphonite (29 g, 90%) having the following constants: B.p. 142-144° at 3 mm; d_4^{20} 0.8809; n_D^{20} 1.4489; found MR_D 96.89; calculated $C_{18}H_{39}O_2P$ MR_D 96.80.

Found %: P 9.64; 9.72
$C_{18}H_{39}O_2P$. Calculated %: P 9.74

The ester does not wet glass.

8. Diphenyl ethylphosphonite. Starting with phenol (31.8 g), pyridine (23.8 g) and ethylphosphonous dichloride (22.2 g) in an ether medium, we obtained, after the usual treatment and removal of ether, a residue that gave the following fractions on being distilled:

Fr. I, B.p. to 116° at 1.5 mm; 1.5 g
Fr. II, B.p. 116 - 120° at 1.5 mm; 32 g
Fr. III, B.p. 120 - 124° at 1.5 mm; 0.3 g
Residue: 2 g

Refractionation of Fraction II yielded diphenyl ethylphosphonite (30 g, 72.5%) as a colorless liquid having the following constants: B.p. 115-115.5° at 1 mm; n_D^{20} 1.5660; d_4^{20} 1.1050; found MR_D 72.57; calculated $C_{14}H_{15}O_2P$ MR_D 71.13.

Found %: P 12.65; 12.68
$C_{14}H_{15}O_2P$. Calculated %: P 12.58

Addition of Sulfur to Ethylphosphonous Esters

1. Addition of sulfur to diethyl ethylphosphonite. Diethyl ethylphosphonite (5.7 g) and benzene (10 ml) were introduced into a 30-ml three-necked flask fitted with reflux condenser, thermometer, and tube for the passage of carbon dioxide. Finely ground sulfur (1.23 g) was added in small portions to the benzene solution. The sulfur-addition reaction proceeded with great vigor. Fractionation of the reaction product yielded:

Fr. I, B.p. 50 - 80° at 10 mm; 0.5 g
Fr. II, B.p. 80 - 82° at 10 mm; 5.2 g

Further fractionation of Fraction II yielded diethyl ethylphosphonothionate (5.1 g, 74%) having the following constants: B.p. 80.5-81.0° at 10 mm; d_4^{20} 1.0356; n_D^{20} 1.4558; found MR_D 47.82; calculated $C_6H_{15}O_2PS$ MR_D 47.84.

Found %: S 17.62; 17.50
$C_6H_{15}O_2PS$. Calculated %: S 17.57

This ester is a colorless fuming mobile liquid smelling of turpentine.

2. Addition of sulfur to diisopropyl ethylphosphonite. The materials taken for reaction were: diisopropyl ethylphosphonite (4.2 g), benzene (10 ml), and sulfur (0.76 g). Reaction was vigorous. The following fractions were obtained:

Fr. I, B.p. to 66° at 1.5 mm; 0.6 g
Fr. II, B.p. 66 - 69° at 1.5 mm; 3.6 g
Residue 0.5 g

A second fractionation yielded diisopropyl ethylphosphonothionate (2.8 g, 56.5%) as a colorless fuming liquid smelling of turpentine and having the following constants: B.p. 69-70° at 1.5 mm; d_4^{20} 1.0005; n_D^{20} 1.4622; found MR_D 57.80; calculated at $C_8H_{19}O_2PS$ MR_D 57.08.

Found %: P 14.8; 14.72; S 15.05; 15.15
$C_8H_{19}O_2PS$. Calculated %: P 14.75; S 15.2

3. Action of sulfur on diphenyl ethylphosphonite. The materials taken for reaction were diphenyl ethylphosphonite (4.3 g) and sulfur (0.6 g). The reaction, unlike that of the aliphatic esters of ethylphosphonous acid, did not go in the cold. The flask was warmed, and at 40° reaction set in. The temperature rose spontaneously to 120°, and the whole of the sulfur reacted. Distillation yielded a fraction (3.4 g, 69.5%) having the following constants: B.p. 144-145° at 1 mm; d_4^{20} 1.1811; n_D^{20} 1.5771; found MR_D 78.08; calculated $C_{14}H_{15}O_2PS$ MR_D 77.58.

Found %: S 11.36; 11.42; P 11.02; 11.18
$C_{14}H_{15}O_2PS$. Calculated %: S 11.5 P 11.12

4. Addition of sulfur to ethylphosphonous dichloride. The operations were carried out in a stream of carbon dioxide. The materials taken for reaction were ethylphosphonous dichloride (6.2 g) and sulfur (1.5 g). No reaction was observed: the sulfur dissolved when the mixture was heated to 114°, but came out again when the solution was cooled. Introduction of aluminum chloride (0.1 g) into the cold mixture of ethylphosphonous dichloride

and sulfur initiated a vigorous reaction: the temperature rose to 154°, and the liquid in the flask darkened. Distillation yielded a fraction (5.5 g, 71%) having the following constants: B.p. 88.5 - 89° 46 mm; d_4^{20} 1.3550; n_D^{20} 1.5440; found MR_D 37.97; calculated at $C_2H_5PSCl_2$ MR_D 36.56.

Found %: Cl 43.52; 43.68

$C_2H_5PSCl_2$. Calculated %: Cl 43.55

Ethylphosphonothionic dichloride is a colorless fuming liquid of characteristic odor.

Action of Cuprous Iodide on Ethylphosphonous Esters

1. Action of cuprous iodide on dimethyl ethylphosphonite. Dimethyl ethylphosphonite (1.5 g) was placed in a test tube fitted with a tube for passage of carbon dioxide, and cuprous iodide (2.3 g) was gradually added. The temperature rose to 75°, but not all of the cuprous iodide dissolved. The test tube was heated at 140-150° until the whole of the cuprous iodide had dissolved. The reaction product did not crystallize immediately. Its melting point after recrystallization from alcohol was 160-161°.

Found %: P 10.08; 9.90

$C_4H_{11}O_2P \cdot CuI$. Calculated %: P 9.93

2. Action of cuprous iodide on diethyl ethylphosphonite. Cuprous iodide (2.9 g) was added to the ester (2.3 g), and the temperature rose to 77°. The test tube was heated to 140-150°. The crystalline substance obtained melted, after being recrystallized from alcohol, at 167-168°.

Found %: P 9.17; 9.12

$C_6H_{15}O_2P \cdot CuI$. Calculated %: P 9.11

3. Action of cuprous iodide on dipropyl ethylphosphonite. When cuprous iodide (2.0 g) was added to the ester (1.9 g), the temperature rose to 50°. The test tube was heated to 140-150°, and when it was cooled a thick noncrystallizing syrup was obtained.

4. Action of cuprous iodide on diphenyl ethylphosphonite. Cuprous iodide (3.8 g) was added to diphenyl ethylphosphonite (5 g), and the temperature rose by 7°. When the mixture was heated to 150°, practically the whole of the copper salt dissolved. When it was cooled, a thick noncrystallizing syrup was obtained.

Action of Halogen Compounds on Ethylphosphonous Esters

1. Action of ethyl iodide on diethyl ethylphosphonite. The reaction, in this and in the succeeding experiments, was carried out in a stream of carbon dioxide. The ester (5.2 g) and ethyl iodide (0.5 g) were placed in the flask and heated. At 50° the contents of the flask became turbid, owing to separation of crystals, and at 104-105° reaction set in and, although further heating was not applied, the temperature in the flask rose to 140°. The liquid became clear and acquired an iodine color. Distillation yielded a fraction (4.8 g) of b.p. 84-86°/10 mm, and a second distillation gave ethyl diethylphosphinate (4.0 g, 77%) having the following constants: B.p. 87-88° at 12 mm; d_4^{20} 0.9983; n_D^{20} 1.4553; found MR_D 39.27; calculated for $C_6H_{15}O_2P$ MR_D 39.13.

Found %: P 20.57; 20.61

$C_6H_{15}O_2P$. Calculated %: P 20.65

2. Action of butyl bromide on diethyl ethylphosphonite. The reaction was carried out with 3 g of the ester and 2.8 g of butyl bromide. Separation of ethyl bromide began at 102-105°, and the temperature was finally raised to 150° and maintained at this value for 40 minutes. After three distillations, ethyl butylethylphosphinate (0.8 g) was isolated; it had the following constants: B.p. 106-108° at 10 mm; n_D^{20} 1.4382; d_4^{20} 0.9932; found MR_D 47.09; calculated for $C_8H_{19}O_2P$ MR_D 48.36.

Found %: P 17.15; 17.31

$C_8H_{19}O_2P$. Calculated %: P 17.40

3. Action of propyl iodide on dipropyl ethylphosphonite. The reaction was carried out with 3 g of the ester and 0.6 g of propyl iodide. Reaction set in at 116-118° and, although heating was discontinued, the temperature rose to 145°. The flask was then heated at 150° for 30 minutes. Two distillations yielded propyl ethylpropylphosphinate (1.09 g) having the following constants: B.p. 104-105° at 8 mm; d_4^{20} 0.9657; n_D^{20} 0.4370;) found MR_D 48.35; calculated for $C_8H_{19}O_2P$ MR_D 48.37.

Found %: P 17.19; 17.12

$C_8H_{19}O_2P$. Calculated %: P 17.40

4. Action of carbon tetrachloride on dimethyl ethylphosphonite. The ester (3.1 g) was placed in a flask, and carbon tetrachloride (4 g) was carefully added dropwise under stirring. Reaction was very vigorous, and the rate of addition was regulated so that the temperature in the flask did not exceed 50-60°. When addition was complete, the flask was heated on the water bath for 20 minutes. Fractionation yielded methyl ethyltrichloromethylphosphinate (1.3 g) having the following constants: B.p. 80-81° at 2.5 mm; d_4^{20} 1.4174; n_D^{20} 1.4889; found MR_D 45.92; calculated for $C_4H_8O_2PCl_3$ MR_D 44.50.

Found %: P 14.02; 14.00
$C_4H_8O_2PCl_3$. Calculated %: P 13.98

The ester is a colorless, mobile liquid.

5. Action of carbon tetrachloride on diethyl ethylphosphonite. Starting with the diethyl ester (4.3 g) and carbon tetrachloride (4.5 g), we obtained, after distillation, ethyl ethyltrichloromethylphosphinate (1.6 g) as a colorless liquid having b.p. 83-84° at 1.5 mm; d_4^{20} 1.3476; n_D^{20} 1.4819; found MR_D 50.66; calculated for $C_5H_{10}O_2PCl_3$ MR_D 49.11.

Found %: P 13.15; 13.0
$C_5H_{10}O_2PCl_3$. Calculated %: P 12.97

6. Action of carbon tetrachloride on dipropyl ethylphosphonite. The ester (4.0 g) and carbon tetrachloride (3.5 g) reacted very vigorously (during the reaction, the temperature was kept within the range 60-70°) and yielded propyl ethyltrichloromethylphosphinate (2.1 g) as a thick, colorless liquid having the following constants: B.p. 88-89° at 1.5 mm; d_4^{20} 1.2790; n_D^{20} 1.4674; found MR_D 55.03; calculated for $C_6H_{12}O_2PCl_3$ MR_D 53.73.

Found %: P 12.35; 12.5
$C_6H_{12}O_2PCl_3$. Calculated %: P 12.26

7. Action of ethyl chloroacetate on diethyl ethylphosphonite. Diethyl ethylphosphonite (3.7 g) and ethyl chloroacetate (4.5 g) were taken for reaction. The flask was heated on a bath, and, when the temperature in the flask was 103-104°, reaction set in and the temperature in the flask rose to 145°. The bath temperature was raised to 150° and maintained at that value for 30 minutes; separation of ethyl chloride stopped. Fractionation yielded a fraction (3.8 g) of b.p. 96-98°/1 mm, and a second fractionation yielded ethyl (ethoxycarbonylmethyl)ethylphosphinate (3.3 g, 65%) having the following constants: B.p. 96-96.5° at 1 mm; d_4^{20} 1.0935; n_D^{20} 1.4443; found MR_D 50.84; calculated for $C_8H_{17}O_4P$ MR_D 50.02.

Found %: P 15.1; 15.12
$C_8H_{17}O_4P$. Calculated %: P 14.9

This ester is a colorless liquid of pleasant odor.

8. Action of ethyl chloroacetate on dipropyl ethylphosphonite. Dipropyl ethylphosphonite (4 g) and ethyl chloroacetate (2.8 g) were taken for reaction. Reaction set in when the temperature in the flask reached 105-106°, and the temperature then rose rapidly to 145°. The flask was then heated at 150° for 30 minutes. Fractionation yielded propyl (ethoxycarbonylmethyl)ethylphosphinate having the following constants: B.p. 104-105° at 1 mm; d_4^{20} 1.0649; n_D^{20} 1.4420; found MR_D 55.45; calculated for $C_9H_{19}O_4P$ MR_D 54.64.

Found %: P 13.8; 13.75
$C_9H_{19}O_4P$. Calculated %: P 13.95

This ester is a colorless liquid of pleasant odor.

Action of Diethylcarbamoyl Chloride on Ethylphosphinous Esters

1. Action of diethylcarbamoyl chloride on diethyl ethylphosphonite. The reaction was carried out in an atmosphere of carbon dioxide. The ester (3.3 g) was heated with the acid chloride (3 g), and reaction set in at 74-76° with separation of ethyl chloride. The temperature of the bath was raised to 150° in the course of one hour and was maintained at that temperature for 40 minutes. Distillation yielded a fraction (2.6 g) of b.p. 108-111°/2.5 mm. A second distillation yielded the diethylamide of ethoxy(ethyl)phosphinylformic acid (1.8 g) having the following constants: B.p. 106-107° at 1.5 mm; d_4^{20} 1.0535; n_D^{20} 1.4625; found MR_D 56.59; calculated for $C_9H_{20}O_3PN$ MR_D 57.69.

Found %: P 13.95; 13.91
$C_9H_{20}O_3PN$. Calculated %: P 14.03

This compound is a colorless, odorless liquid.

2. Action of diethylcarbamoyl chloride on dipropyl ethylphosphonite. The ester (4.5 g) was heated with the acid chloride (3.4 g), and reaction set in at 104° and caused the temperature to rise further to 140°. The flask was heated at 140-145° for 30 minutes. Distillation yielded a fraction (3.5 g) of b.p. 110-114°/1 mm, and a second distillation yielded the diethylamide of ethyl(propoxy)phosphinylformic acid (2.7 g) having the following constants: B.p. 109-110° at 1 mm; d_4^{20} 1.0341; n_D^{20} 1.4597; found MR_D 62.20; calculated for $C_{10}H_{22}O_3PN$ MR_D 61.21.

Found %: P 13.19
$C_{10}H_{22}O_3PN$. Calculated %: P 13.19.

This ester is a colorless, mobile liquid.

SUMMARY

1. By the action of alcohols on ethylphosphonous dichloride in presence of pyridine or triethylamine we have synthesized the following esters, which have not been described previously: the dimethyl, diethyl, dipropyl, diisopropyl, dibutyl, dihexyl, dioctyl, and diphenyl esters of ethylphosphonous acid.

2. Ethylphosphonous esters, being tervalent phosphorus derivatives, readily undergo addition reactions: they combine readily with sulfur, give complex compounds with cuprous iodide, and are very readily oxidized.

3. It has been shown that ethylphosphonous dichloride combines with sulfur in presence of aluminum chloride as catalyst.

4. A study has been made of the rearrangement of ethylphosphonous esters under the influence of alkyl halides, carbon tetrachloride, ethyl chloroacetate, and diethylcarbamoyl chloride. The reaction follows the scheme of the A. E. Arbuzov rearrangement.

5. Syntheses have been carried out for the first time of ethylphosphonothionic esters, dialkylphosphinic esters, ethyltrichloromethylphosphinic esters, (ethoxycarbonylmethyl)ethylphosphinic esters, and diethylamides of alkoxy(ethyl)phosphinylformic acids.

LITERATURE CITED

[1] A. E. Arbuzov, Dissertation, Kazan (1914); A. E. Arbuzov, J. Russ. Chem. Soc., 42, 395 (1910); A. E. Arbuzov, J. Gen. Chem., 4, 898 (1934); A.E. Arbuzov, Gilm Kamai, and O. N. Belorossova, J. Gen. Chem., 15, 766 (1945); A. E. Arbuzov and A. I. Razumov, Bull. Acad. Sci., U.S.S.R., Div. Chem. Sci., 167 (1945); Z. L. Khisamova and Gilm Kamai, J. Gen. Chem., 7, 1162 (1950). *

[2] Gilm Kamai and E. A. Gerasimova, Trans. Kazan, Chem. Tech. Inst., 15, 26 (1950).

[3] R. B. Fox., J. Am. Chem. Soc. 9, 4147 (1950).

[4] M. S. Kharasch, E. V. Jensen and S. Weinhouse, J. Am. Chem. Soc., 14, 429 (1949).

[5] F. Guichard, Ber., 32, 1572 (1899).

[6] Gilm Kamai and L. P. Egorova, J. Gen. Chem., 16, 1521 (1946); Proc. Acad. Sci. U.S.S.R. 55, 223 (1947); Gilm Kamai J. Gen. Chem., 18, 440 (1948).

[7] A. E. Arbuzov and A. A. Dunin, J. Russ. Chem. Soc., 46, 295 (1914).

Received June 23, 1952

A. E. Arbuzov Chemical Institute of the
Kazan Affiliated Institute of the
U.S.S.R. Academy of Sciences

---

* See Consultants Bureau translation, p. 1207

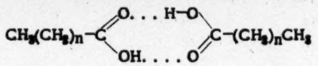
VISCOSITY-STRUCTURE RELATIONSHIP FOR PHOSPHOROUS, PHOSPHORIC, PHOSPHOROTHIONIC, AND BORIC ESTERS

B. A. Arbuzov and V. S. Vinogradova

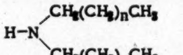
Staudinger and coworkers have found, in a series of investigations [1], that for dilute solutions of organic substances having linear molecules there is a direct relationship between viscosity and chain length. For basal molar solutions of alkanes this relationship may be expressed by the equation:

$$\eta_{sp}(1.4\%) = n \cdot y,$$

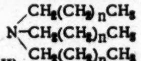
where η_{sp} is the specific viscosity, n is the number of links in the chain, and y is the specific viscosity per member of the chain for the given solvent (1.3×10^{-3} for benzene and 1.5×10^{-3} for carbon tetrachloride) [2]. By the aid of this relation Staudinger, in a number of investigations, drew inferences concerning the configurations of organic molecules in dilute solutions. Thus, Staudinger found from viscosity measurements that the higher fatty acids are present in solution in the form of extended double molecules [3]:



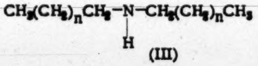
also [4], secondary and tertiary amines are present in solution not in the forms I and II, but in the extended forms III and IV:



(I)

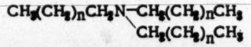


(II)



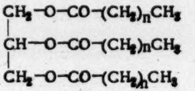
$$CH_3(CH_2)_nCH_2-\underset{\underset{H}{|}}{N}-CH_2(CH_2)_nCH_3$$

(III)



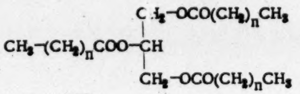
(IV)

Similar extended molecules were found by Staudinger also for acid anhydrides [5], esters of dibasic acids [6], and esters of glycerol (form VI, not V):



$$\begin{array}{l} CH_2-O-CO-(CH_2)_nCH_3 \\ | \\ CH-O-CO-(CH_2)_nCH_3 \\ | \\ CH_2-O-CO-(CH_2)_nCH_3 \end{array}$$

(V)

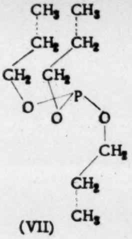


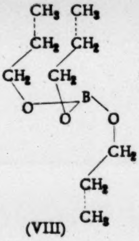
$$\begin{array}{r} CH_2-OCO(CH_2)_nCH_3 \\ | \quad\quad\quad\quad\quad\quad \\ CH_3-(CH_2)_nCOO-CH \quad\quad\quad\quad\quad\quad \\ | \quad\quad\quad\quad\quad\quad \\ CH_2-OCO(CH_2)_nCH_3 \end{array}$$

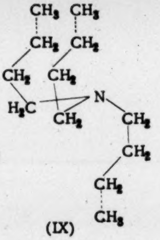
(VI)

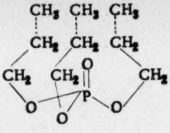
We have found in our previous investigations [8] that the parachor can give us an idea of the way in which the chains are disposed in organic compounds of certain type. Thus, according to parachor data on phosphorous esters, only two of the three chains are disposed parallel to one another (VII) [9, 12]. A similar picture is presented by boric esters (VIII) [10] and by tertiary amines (IX) [11]: (see top of next page). However, the parachor indicates that in phosphoric esters (X) and phosphorothionic esters [12] the three chains are disposed in parallel array. It was of interest to compare the conclusions derived from these parachor data with those derived from viscosity measurements. For tertiary amines [11] parachor and viscosimetric [4] measurements gave similar results.

In the present communication we give results of viscosimetric measurements that we have made on phosphorous, phosphoric, phosphorothionic, and boric esters, chosen, in each case, so as to have ether chains of sufficient length. The results obtained for phosphorous esters are given in Table 1.


(VII)


(VIII)


(IX)


(X)

Comparison of the values of η_{sp}(1.4%) and Z_η found experimentally with those calculated for a parallel disposition of only two chains (−P=) and for a parallel disposition of all three chains (P≡) shows quite clearly that, according to viscosity data, in dilute solution trialkyl phosphites have only two parallel chains, which is in accord with parachor data.

The results of viscosity determinations on boric esters are summarized in Table 2.

The viscosity data for boric esters definitely indicate molecules of extended form having only two ester chains disposed in parallel fashion, which is in accord with parachor data. The results of viscosity measurements on phosphoric and phosphorothionic esters are given in Table 3.

As the results in Table 3 show, the values of η_{sp} (1.4%) and Z_η indicate an extended form of molecule for phosphoric and phosphorothionic esters in dilute solution and are thus at variance with parachor data for these compounds, according to which all the three esters interact with one another. The nonaccord of these conclusions concerning the structures of phosphoric and phosphorothionic esters makes it desirable to carry out further investigation into the questions: In the analysis of parachor data, what do the corrections for parallelism indicate? What does viscosity measurement yield for molecules of branched structure?

TABLE 1

Substance	Sol-vent	Con. (%)	$\eta_{sp}(1.4\%)\cdot10^{-3}$			$Z_\eta\cdot10^{-4}$ *		
			Found (at 20°)	Calcd. for		Found (at 20°)	Calcd. for	
				−P=	P≡		−P=	P≡
Trioctyl phosphite	C_6H_6	2.85 2.48 4.97	28.4 28.8 26.0	24.7	13.0	20.3 20.6 18.6	17.7	9.3
Ditto	CCl_4	2.31 3.19	30.9 33.0	28.5	15.0	22.1 23.5	20.5	10.8
Trinonyl phosphite	C_6H_6	2.93 3.64	25.8 23.9	27.3	14.3	18.4 17.0	19.5	10.2
Ditto	CCl_4	2.77 3.91	28.3 31.3	31.5	16.5	20.2 22.3	22.7	11.9
Tridecyl phosphite	C_6H_6	2.88 3.69	29.8 26.3	29.9	15.6	21.3 18.8	21.4	11.6
Ditto	CCl_4	2.76 3.32	37.4 40.3	34.5	18.0	26.8 28.8	24.8	13.0
Trihexadecyl phosphite	C_6H_6	3.8	40.6	45.5	23.4	29.0	32.5	16.7
Ditto	CCl_4	3.5	51.6	52.5	27.0	36.8	37.8	19.4

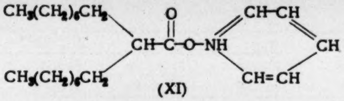
---

* $Z\eta$ is calculated not for basal molar solutions, but for a solution having a concentration in g/liter of $K_{equiv.}$ (which is $0.93\cdot10^{-4}$ for benzene and $1.08\cdot10^{-4}$ for carbon tetrachloride.

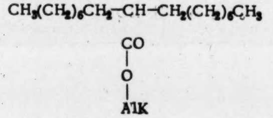
The results of numerous researches by Staudinger and coworkers indicate that, according to viscosity data, molecules have an extended form in solutions. The results of Staudinger [13] according to which the pyridine salt of dioctylacetic acid has the structure XI, which has a nonextended form and not the extended form of a dioctylacetic ester (XII), are not very convincing, for the chains have in each case the same length (17 members*):

---

* If all the atoms of the pyridine ring are considered to be in the chain.



(XI)



(XII)

TABLE 2

Substance	Solvent	Concen. %	$\eta_{sp}(1.4\%)\cdot10^{-3}$ Found at 20°	η_{sp} Calcd. for $-B=$	η_{sp} Calcd. for $B\equiv$	$Z_\eta\cdot10^{-4}$ Found at 20°	Z_η Calcd. for $-B=$	Z_η Calcd. for $B\equiv$
Triheptyl borate	C_6H_6	2.86	23.2	22.1	11.7	16.6	15.8	8.4
		4.63	26.3			18.8		
Ditto	CCl_4	2.96	22.6	25.5	13.5	16.2	18.4	9.7
		2.77	22.8			16.3		
Trioctyl borate	C_6H_6	4.25	26.9	24.7	13.0	19.8	17.7	9.3
Ditto	CCl_4	3.92	25.6	28.5	15.0	18.3	20.5	10.8
		5.56	28.1			20.0		
Trinonyl borate	C_6H_6	2.36	28.5	27.3	14.3	20.4	19.5	10.2
		2.95	26.3			18.8		
Ditto	CCl_4	2.44	36.4	31.5	16.5	26.0	22.7	11.9
		3.72	33.3			23.8		
Tridecyl borate	C_6H_6	3.60	29.2	29.9	15.6	20.8	21.4	11.2
Ditto	CCl_4	2.22	37.9	34.5	18.0	27.1	24.8	13.0
		2.22	38.7			27.6		
		3.15	38.8			27.7		
Tricyclohexyl borate	C_6H_6	3.07	22.3	19.6*	7.4	15.9	14.0*	8.6
		4.17	19.0	19.6	7.4	13.6	14.0	8.6
Trihexadecyl borate	C_6H_6	4.89	49.0	45.5	23.4	35.0	32.6	16.7
Ditto	CCl_4	3.68	50.8	52.5	27.7	36.3	37.8	19.5

---

* The cyclohexyl radical being considered to provide six members of the chain.

Thus, viscosity data give an indication of the length of the longest chain of atoms in the molecule, and it is possible that they do not form an adequate criterion of the disposition of individual chains in the molecule.

From this point of view viscosity measurements on cyclic compounds having a large number of atoms in the ring are of interest. Staudinger and Bauer [14] have published results on the viscosities of large-ring compounds synthesized by Ruzicka.

If it is considered that the viscosity gives the length of the molecule, then for a large ring it should

TABLE 3

Substance	Solvent	Concentration, %	η_{sp} (1.4%)·10^{-3}			$Z\eta\cdot10^{-4}$		
			Found	Calcd. for		Found	Calcd. for	
			at 20°	−P=	P≡	at 20°	−P=	P≡
Trihexyl phosphate	C_6H_6	3.38 3.47	23.8 18.8	19.5	11.7	17.0 13.4	14.0	8.4
Ditto	CCl_4	3.51	19.12	22.5	13.5	13.7	16.2	9.7
Trioctyl phosphate	C_6H_6	1.57 2.53 3.74	26.9 25.2 28.5	24.7	14.3	19.2 18.0 20.4	17.7	10.2
Ditto	CCl_4	3.09 4.51	26.7 27.1	28.5	16.5	19.1 19.3	20.5	11.9
Trihexyl phosphorothionate	C_6H_6	3.69 4.56	21.3 21.3	19.5	11.7	15.2 15.2	14.0	8.4
Ditto	CCl_4	3.40 2.24	25.2 27.1	22.5	13.5	18.0 19.3	16.2	9.7
Trioctyl phosphorothionate	C_6H_6	3.83	27.0	24.7	14.3	19.8	17.7	10.2

correspond to half of the number of members in the ring. Staudinger's results [15] for carbon tetrachloride solutions of large-ring compounds are given in Table 4.

TABLE 4

Substance	No. of members in ring (n)	No. of members in chain of length ∼ n/2	$Z\eta\cdot10^{-4}$			
			Found	Calcd. for n	Calcd. for ∼ n/2	Calcd. for n/2
Cyclopentadecane	15	8	12.0	16.2	8.7	8.6
Methylcyclopentadecane	15	9	14.0	16.2	9.8	8.6
Cyclotriacontane	30	16	30.0	32.4	17.3	16.2
Cyclotriacontanone*	30	17	29.9	32.4	18.4	17.3
1,16-Cyclotriacontanedione	30	18	31.5	32.4	19.4	17.3
1,16-Dimethylcyclotriacontane	30	18	29.1	32.4	19.4	17.3
Cyclotetratriacontane	34	18	32.2	36.8	19.4	18.3
Cyclotetratriacontanone	34	19	31.4	36.8	20.5	19.4

---

* A methyl side chain or a carbonyl group lengthen the chain by unity.

In the column headed "$Z_\eta\cdot10^{-4}$ calcd. for ∼n/2" Staudinger gives values of Z_η for paraffins having chains of approximately n/2 members. In the last column we have given values of Z_η calculated for n/2*. In the first paper [14] Staudinger regards the difference between the value of η_{sp} found for these large-ring compounds and that calculated for n/2 as the ring increment, and he points out that it is impossible to say from the results obtained whether there is a simple relation between the value of the ring increment and the number of members of the ring.

In the later article [15], from which Table 4 is taken, Staudinger does not refer to the ring increment, but explains the large discrepancy (between the value of Z_η calculated for n/2 and the value of Z_η found) on the hypothesis that the parallel arrangement of the two halves of the ring renders them more rigid: they therefore

---

* Treating methyl and carbonyl each as one member of the chain.

TABLE 5

Substance	Solvent	No. of members (n)	Concen. %	η_{sp} (1.4%)·10^{-3}		$Z_\eta \cdot 10^{-4}$	
				Found at 20°	Calcd. for n	Found	Calcd. for n
Triethylene glycol ester of succinic acid	C_6H_6	14	3,46	32.6	18.2	23.3	13.1
		14	5.14	32.0	18.2	22.9	13.1
		14	3.22	29.9	18.2	20.7	13.1
Ditto	CCl_4	14	3.33	33.8	21.0	24.1	15.1
		14	5.19	33.3	21.0	23.8	15.1
1,3-Propanediol ester of sebacic acid	C_6H_6	15	2.42	29.3	19.5	21.0	13.9
		15	5.72	26.6	19.5	18.7	13.9
Ditto	CCl_4	15	3.76	30.7	22.5	21.9	16.2
		15	3.71	29.7	22.5	21.2	16.2
Triethylene glycol ester of adipic acid	C_6H_6	16	2.43	28.2	20.8	20.1	14.9
		16	4.30	31.7	20.8	22.7	14.9
		16	5.75	30.1	20.8	21.5	14.9
Ditto	CCl_4	16	4.55	36.2	24.0	25.8	17.3
		16	5.00	36.1	24.0	25.7	17.3
Diethylene glycol ester of sebacic acid	C_6H_6	17	3.72	31.8	22.1	23.3	15.8
Triethylene glycol ester of sebacic acid	C_6H_6	20	4.19	30.1	26.0	21.5	18.6
		20	6.14	31.7	26.0	22.7	18.6
Ditto	CCl_4	20	2.70	39.6	30.0	28.3	21.6
		20	3.46	40.2	30.0	28.7	21.6

shorten to a less extent than the paraffins having n/2 chain members, i.e., they have a greater viscosimetric length than paraffin molecules having n/2 members. Also, a comparison of the values given in Table 4 of $Z\eta$ found and $Z\eta$ calculated for n members in the ring indicates that these data are fairly close together, and it is quite possible that in this case also the viscosity indicates the longest chain of atoms in the molecule, all the atoms forming part of the chain being counted.

In order to extend the data available on the viscosity of large-ring compounds, we have prepared cyclic esters having a large number of members in the ring, and we have measured their viscosities. It must be remarked, however, that in this case we have not succeeded in obtaining results that are in good agreement; an increase in accuracy is called for. Results of measurements in carbon tetrachloride are given in Table 5.

The results in Table 5 show that the experimental values for the viscosities of large-ring esters are considerably higher than those calculated for the total number of members in the ring. There is no explanation for this at present.

It should be noted that a similar exaltation of the experimental viscosity values in comparison with the calculated values was observed by Staudinger in the case of substituted amides of higher fatty acids [16]; in chloroform solvent the exaltation was 14 units. This exaltation was ascribed by Staudinger to the effect of the amide group.

EXPERIMENTAL

The specific viscosity of the compounds investigated was determined from the usual formula:

$$\eta_{sp} = \frac{t_2 \cdot d_2}{t_1 \cdot d_1} - 1,$$

where t_1, d_1 and t_2, d_2 are the times of flow and the densities for the pure solvent and for the solution. The viscosity measurements were carried out in an open viscometer similar to that used by Staudinger [17]. The volumes of the bulbs of the viscometer were 1 and 10 ml respectively, the diameter of the capillary was 0.18 mm, and its length was 95 mm. Cryoscopic benzene, freshly distilled over sodium, and carbon tetrachloride were chosen as solvents; their times of flow in our viscometer were about 300 and 250 seconds respectively.

The measurements were carried out in a thermostat at 20° (± 0.1°). A solution of volume 10 ml and concentration not exceeding 3-5 wt.-% was prepared. The lower limit of concentration was chosen so that the difference in the times of flow of the solution and of the pure solvent should not be less than ten seconds. By means of a pipet, 3 ml of the solution was introduced through a sintered glass filter into the lower bulb. The time of flow was measured to the nearest 0.1 sec. the measurement being repeated five or six times and the mean value determined. The divergence in the readings did not exceed 0.2-0.4 sec. The air that entered the apparatus as liquid flowed out was dried over phosphoric anhydride in a five-liter bottle.

The phosphorous esters, prepared by transesterification of triethyl phosphite with the corresponding alcohols, were:

1. Trioctyl phosphite: b.p. 212-214°/2 mm; n_D^{20} 1.4475; d_4^{20} 0.8907 [12].
2. Trinonyl phosphite: b.p. 226.5-227.5°/1 mm; n_D^{20} 1.4495; d_0^{20} 0.8879 [12].
3. Tridecyl phosphite: b.p. 236.5-237.5/1.5 mm; n_D^{20} 1.4518; d_0^{20} 0.8842 [12].
4. Trihexadecyl phosphite: b.p. 288-290°/0.4 mm, m.p. 51° [18].

The boric esters, prepared, apart from No. 8 and No. 9, by reaction of the corresponding alcohol with boric acid, were:

5. Triheptyl borate: b.p. 185-186°/2 mm; n_D^{20} 1.4280; d_4^{20} 0.8398 [8].
6. Trioctyl borate: b.p. 200-201°/2 mm; n_D^{20} 1.4360; d_4^{20} 0.8548 [8].
7. Tridecyl borate: b.p. 274-276°/0.5 mm; n_D^{20} 1.4440; d_4^{20} 0.8581 [8].
8. Tricyclohexyl borate, prepared by transesterification of butyl borate: b.p. 153-155°/2 mm; d_0^{40} 0.9567 [8].
9. Trinonyl borate, prepared for the first time by heating boric acid (1 g) with nonyl alcohol (b.p. 92-94°/8 mm) (8 g) and then driving off water under vacuum. After two redistillations: b.p. 228-230°/1.5 mm; n_D^{20} 1.4405; d_4^{20} 0.8575.

Found %: B 2.25
$C_{27}H_{57}O_3B$. Calculated %: B 2.34

10. Trihexadecyl borate: b.p. 328-329°/< 0.5 mm; m.p. 43-44° [18].

The phosphoric esters, prepared by the action of phosphoryl chloride on the corresponding alcohols in presence of pyridine [19], were:

11. Trihexyl phosphate: b.p. 187-188°/2 mm; n_D^{20} 1.4340; d_0^{20} 0.9396 [12].
12. Trioctyl phosphate: b.p. 225-227°/2 mm; n_D^{20} 1.4410; d_0^{20} 0.9200 [12].

The phosphorothionic esters, prepared by addition of sulfur to the corresponding phosphite, were:

13. Trihexyl phosphorothionate: b.p. 188-188.5/2.5 mm; n_D^{20} 1.4568; d_0^{20} 0.9501 [12].
14. Trioctyl phosphorothionate: b.p. 224-226°/< 0.5 mm; n_D^{20} 1.4592; d_0^{20} 0.9293 [12].

The remaining esters were:

15. Trimethylene sebacate: b.p. 145-147°/4 mm; n_D^{20} 1.4700; d_0^{60} 1.0405 [20].
16. Diethylene glycol ester of sebacic acid: b.p. 175-178°/3.5-4 mm; d_0^{60} 1.0650 [8,20].

17, 18, and 19. Cyclic esters of dibasic acids, the preparations of which are given below.

Preparation of the cyclic ester of triethylene glycol with adipic acid. Adipic acid (30 g) and triethylene glycol (b.p. 149-150°/4 mm) (33 g) were heated together for two hours at a bath temperature of 220° in a small flask having an outlet tube. Some water separated, and heating was then continued at a bath temperature of 220-230° under reduced pressure (15 mm for one hour and then 5 mm for 30 minutes). The polyester obtained formed a thick dark mass. It was depolymerized by Carothers' method [20], which was modified by the use of an aluminum block in which a hole had been drilled to carry the reaction vessel (diameter of block 14 cm, height 17 cm; diameter of hole 7 cm, depth 15 cm); the block was provided with a nichrome-wire winding for heating purposes and was lagged with asbestos. The modification permitted the more ready maintenance of a constant high temperature. Depolymerization was carried out in a cylindrical glass vessel having a narrow neck and a fused-on delivery tube. The vessel was placed in the hole in the block, and the space between the vessel and the wall of the hole was packed with fine copper filings, in which a thermometer was placed. With such an aluminum block it was found possible by the aid of a rheostat to maintain a temperature constant to 1-2° in the range 250-300°. This arrangement is safe in use and enables the desired temperature to be maintained without the use of selected liquids of the required boiling point, as described by Carothers.

The polyester from triethylene glycol and adipic acid was placed in the depolymerization vessel, and the catalyst ($SnCl_2 \cdot 2H_2O$, 0.5 g) was added. Depolymerization was carried out at a block temperature of 250-270° and under a pressure of 3-4 mm. Depolymerization was rapid: 40 g of distillate was obtained in 3 hrs 30 min. Redistillation of the distillate gave a fraction (23 g) of b.p. 192-195°/5 mm which rapidly crystallized. After a further redistillation the fraction boiled at 172-174°/2.5 mm and yielded a slightly yellowish liquid, which crystallized immediately. The cyclic ester has a powerful, persistent, tarry odor.

Found: M 260
$C_{12}H_{20}O_6$. Calculated: M 260 (Rast's method)

Found %: C 55.59; H 7.54
$C_{12}H_{20}O_6$. Calculated %: C 55.38; H 7.74

Preparation of the cyclic ester of triethylene glycol with succinic acid. Succinic acid (23.5 g) and triethylene glycol (33 g) were heated together for two hours at a bath temperature of 200-210°, for one hour under 12 mm at 220°, and then for 30 minutes under 2 mm at 225°. The polyester formed was a thick, immobile mass. Depolymerization was carried out in the previously described apparatus; the catalyst was $SnCl_2 \cdot 2H_2O$ (0.5 g) and the block temperature was 272-275°. The reaction was complete in 3 hrs 30 min; the pressure at the beginning of the depolymerization was 2.5 mm, but rose towards the end to 6 mm. The distillate (46 g) was a golden-yellow liquid.

Fractionation gave:

Fraction 1, b.p. 110-163°/3 mm - 10 g.
Fraction 2, b.p. 163-168°/3 mm - 33 g.

A second fractionation of Fraction 2 gave a product of b.p. 169-170°/3 mm (28 g); it was a thick yellowish liquid having a tarry odor. On the next day it had crystallized (m.p. 54-55°). The melting point after recrystallization from methanol was 57-58°.

Found: M 254
$C_{10}H_{16}O_6$. Calculated: M 232 (Rast's method)

Found %: C 51.49; H 6.80
$C_{10}H_{16}O_6$. Calculated %: C 51.71; H 6.94

Preparation of the cyclic ester of triethylene glycol with sebacic acid. Sebacic acid (10 g) and triethylene glycol (8.0 g) were heated together for two hours at 210-220°, for one hour at 220° under 15 mm pressure, and then for 30 minutes at 220-230° under 3 mm. Depolymerization was carried out in presence of $SnCl_2 \cdot 2H_2O$ at 265-270° under 3 mm pressure. Depolymerization was slow (one drop per minute, and towards the end, one gram per hour), and the total distillate was 12 g. Fractionation gave a fraction of b.p. 202-204° (uncorr.)/3 mm (3 g). It was a thick liquid; when it was rubbed out on the hand there was a persistent, unpleasant odor, reminiscent of musk.

Found %: C 60.61; H 8.74
$C_{16}H_{28}O_6$. Calculated %: C 60.79; H 8.93

SUMMARY

1. The specific viscosities have been determined of dilute solutions in benzene and in carbon tetrachloride of phosphorous and boric esters having long hydrocarbon radicals (from octyl to decyl). Comparison of the values found for η_{sp} (1.4%) and $Z\eta$ with those calculated indicates that the molecules of these esters are in the extended form in dilute solution, which is in agreement with parachor data.

2. The specific viscosities have been determined of dilute solutions in benzene and in carbon tetrachloride of phosphoric and phosphorothionic esters having hexyl and octyl radicals. Comparison of the values found for η_{sp} (1.4%) and $Z\eta$ with those calculated indicates that the molecules of phosphoric and phosphorothionic esters are in the extended form in dilute solution, which is not in agreement with conclusions based on a study of the parachors of these esters.

3. When a comparison is made of the found and calculated values of η_{sp} (1.4%) and $Z\eta$ for macrocyclic compounds having rings of 15-34 members for which viscosity data are available in the literature, it is found that the viscosity values found are closer to those calculated for the total number of members in the ring than to those calculated, following Staudinger's views, for a half of that number.

4. Cyclic esters of triethylene glycol with succinic, adipic, and sebacic acids have been synthesized, and viscosity measurements have been made on their dilute solutions. The values found for η_{sp} (1.4%) and $Z\eta$ are greater than those calculated for the total number of members in the ring.

5. Our results show that further investigation is required into the question of what measurements of viscosity tell us concerning molecules of branched structure and molecules having branched rings, and they show that further investigation is required also into the nature of Gibling's corrections for parallelism in the determination of molecular structure by the parachor method.

Received January 5, 1952

A. M. Butlerov Chemical Research Institute attached to
the V. I. Ulyanov-Lenin Kazan State University

LITERATURE CITED

[1] H. Staudinger, "Macromolecular Organic Compounds. Rubber and Cellulose", United Sci. Tech. Press, 1935, p. 57; H. Staudinger and F. Staiger, Ber. 68, 707 (1935); H. Staudinger and H. Schwalenstocker, ibid. 727; H Staudinger and A. Steinhoper, ibid, 471, Ann. 517,56 (1935).

[2] H. Staudinger and H. Schwalenstocker, Ber. 68, 728 (1935).

[3] H. Staudinger and E. Ochiai, Z. phys. Chem. 158, 45 (1932).

[4] H. Staudinger and K. Rossler, Ber. 69, 52 (1936).

[5] H. Staudinger and H. Schwalenstocker, Ber. 68, 727 (1935).

[6] Ibid, p. 742.

[7] Ibid, p. 746.

[8] V. Vinogradova, Sci. Mem. Kazan Univ. 110, Book 9, (1950).

[9] B. A. Arbuzov and V. S. Vinogradova, Ibid., p. 21.

[10] B. A. Arbuzov and V. S. Vinogradova, Proc. Acad. Sci. USSR, 55, 415 (1947).

[11] B. A. Arbuzov and L. M. Guzhavina, Proc. Acad. Sci. USSR, 61, 63 (1948).

[12] B. A. Arbuzov and V. S. Vinogradova, Bull. Acad. Sci. USSR Div. Chem. Sci. 733 (1951).

[13] H. Staudinger, "Macromolecular Organic Compounds", United Sci. Tech. Press, 1935, p. 78

[14] H. Staudinger and R. C. Bauer, Helv. Chim. Acta 17, 863 (1934).

[15] H. Staudinger, Makromol. Chem. 4, 289 (1950).

[16] H. Staudinger and Rossler, Ber. 69, 63 (1936).

[17] H. Staudinger and Steiger, Ber. 68, 707 (1935).

[18] B. A. Arbuzov and V. S. Vinogradova, Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 3, 505 (1952).*

[19] T. Milobendzky, A. Sachnowsky, Ch. Polsky, 15, 34 (1917).

[20] W. Carothers, J. Am. Chem. Soc. 57, 931 (1935).

---

* See Consultants Bureau translation, p. 483.

DIPOLE MOMENTS OF N,N-DIETHYL(DIALKOXYPHOSPHINYL)FORMAMIDES

B. A. Arbuzov and T. G. Shavsha

N,N-Diethyl(dialkoxyphosphinyl)formamides form an interesting group of quinquevalent phosphorus derivatives containing adjoining P=O and $O=C-NR_2$ groups. There are no available data on the dipole moments of these substances, and we considered that it would be of interest to determine these properties.

The disposition of the individual bond moments in N,N-diethyl(dialkoxyphosphinyl)formamides is similar to that found in phosphoric esters. This circumstance makes it possible for us to discuss a number of possible structures for N,N-diethyl(dialkoxyphosphinyl)formamides, the spatial arrangement of individual groups, and the possibility of the movement of certain groups around the appropriate bonds as axes. We have measured the dipole moments of six N,N-diethyl(dialkoxyphosphinyl)formamides [1], and have obtained the results given in Table 1.

TABLE 1

No.	Substance	Dipole moment (D)
1	$(C_2H_5O)_2-\underset{\underset{O}{\Vert}}{P}-\underset{\underset{O}{\Vert}}{C}N(C_2H_5)_2$	2.91
2	$(n\text{-}C_3H_7O)_2-\underset{\underset{O}{\Vert}}{P}-\underset{\underset{O}{\Vert}}{C}-N(C_2H_5)_2$	3.02
3	$(i\text{-}C_3H_7O)_2-\underset{\underset{O}{\Vert}}{P}-\underset{\underset{O}{\Vert}}{C}-N(C_2H_5)_2$	2.88
4	$(n\text{-}C_4H_9O)_2-\underset{\underset{O}{\Vert}}{P}-\underset{\underset{O}{\Vert}}{C}-N(C_2H_5)_2$	3.09
5	$(i\text{-}C_5H_{11}O)_2-\underset{\underset{O}{\Vert}}{P}-\underset{\underset{O}{\Vert}}{C}-N(C_2H_5)_2$	2.92
6	$(C_6H_{13}O)_2-\underset{\underset{O}{\Vert}}{P}-\underset{\underset{O}{\Vert}}{C}-N(C_2H_5)_2$	2.94

From the results given in Table 1 it will be seen that the dipole moments of N,N-diethyl(dialkoxyphosphinyl)formamides vary from 2.88 D to 3.09 D, the mean value for the homologous series being 2.96 D, which is practically the same as the mean value of the dipole moments of phosphoric esters, $O{=}{=}P-(OR)_3$, which is 3.08 D for the homologous series [2].

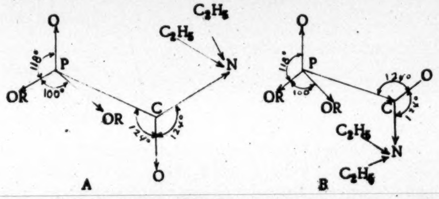


Fig. 1

The molecule of an N,N-diethyl(dialkoxyphosphinyl) formamide may be represented by the following two configurations (A and B in Fig. 1, which represent two possible arrangements of the group $-\underset{\underset{O}{\Vert}}{C}-NR$ with respect to the bond P—C.

In the construction of molecular configurations for an N,N-diethyl(dialkoxyphosphinyl)formamide, the valency angles in O=C—P and O=C—N are taken as 124°, this assumption being based on the constant valency angle of approximately 124° that is observed for the group O=C—X in studies by the electronographic method of valency angles in various compounds containing doubly bound carbon.

We assume the configuration of the diethylamido group to be similar to that of trimethylamine, which has been established by electronographic methods [3]: the nitrogen valency angle is taken as 108°.

The dipole moment of the N,N-diethyl(dialkoxyphosphinyl)formamide molecule calculated by the Smyth-Lewis formula [4], free rotation being assumed for the group OR around the bond P—O at an angle of 70° and for the groups $-\underset{\underset{O}{\Vert}}{C}-N(C_2H_5)_2$ around P—C, is 3.33 D.

The dipole moment of the P=O bond is assumed to be 3.5 D, the value 1.2 D is assumed for P—O, 1.12 D is assumed for O—R, 0.9 D for P—C, 2.3 D for C=O and 0.8 D for the group $-\underset{\underset{O}{\Vert}}{C}-N(C_2H_5)_2$ [3]. The angle O=P—O is assumed to be 118°, the angle O–P–O to be 100°, and the oxygen angle to be 110°, as in phosphoric esters [8].

Thus, the dipole moment of this molecule calculated on the assumption of free rotation of the irregular groups OR and $-\underset{\overset{\|}{O}}{C}-N(C_2H_5)_2$, exceeds the experimentally found value by only 0.37 D.

However, the agreement between the value of the dipole moment calculated for completely free rotation and that found experimentally does not altogether prove the presence of free rotation. Thus, the calculations we have made for orthocarbonic, orthosilicic, orthotitanic, phosphorous, and phosphoric esters of interatomic distances of individual groups on the assumption of free rotation, taking into account the radius of action of Van der Waals forces due to methyl and methylene groups, show that for these esters it is doubtful whether free rotation of the irregular groups is possible, for there is a great measure of superposition of Van der Waals spheres of action associated with methyl or methylene groups of adjacent alkoxy chains [5].

For N,N-diethyl(dialkoxyphosphinyl)formamides the configurations C and D (Fig.2) show the greatest overlap in the Van der Waals spheres of influence associated with alkoxy groups and are therefore of low probability for any position of the group $-\underset{\overset{\|}{O}}{C}-N(C_2H_5)_2$. The calculated dipole moments for the configurations C and D are 5.36 D and 1.76 D respectively.

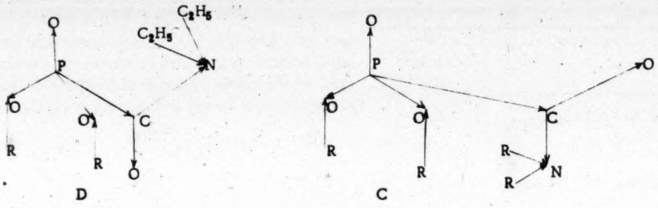


Fig. 2

Configurations of the molecule in which the OR groups are arranged in a plane perpendicular to the paper and to the bond P==O (A_1 and B_1, Fig.3) do not show overlap overlap of Van der Waals spheres of action. The dipole-moment values are 4.00 D for configuration A_1, and 2.09 D for configuration B_1. Configurations A_2 and B_2 (Fig.4) also do not show overlap of Van der Waals spheres of action, and the respective dipole-moment values are 3.46 D and 2.53 D.

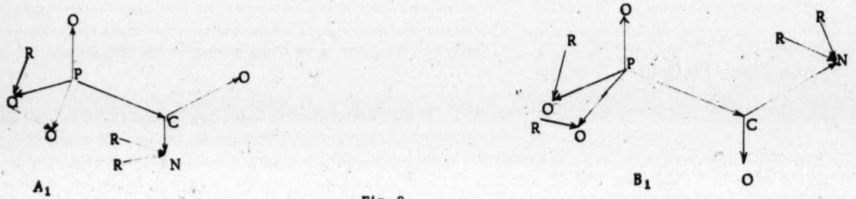
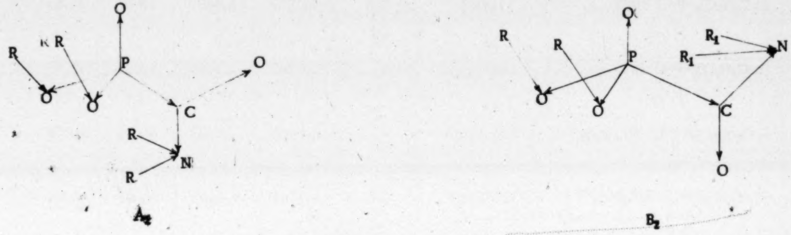


Fig. 3

Thus, if we take into account the interatomic distances and the radius of the sphere of action of Van der Waals forces, which is equal to 2.0 A, we find that the alkoxy groups instead of having free rotation, can have only synchronous vibration about the P–O bond, the O–R groups then being found to lies either in planes perpendicular to the plane of the P–O bond, or in the plane of the P–O bond (Fig. 3 and 4, configurations A_1 and B_1, and A_2 and B_2). The value of the dipole moment averaged over the configurations A_1 and B_1, A_2 and B_2 (in which the two positions described above, for the group $-\underset{\overset{\|}{O}}{C}-N(C_2H_5)_2$ are taken into account) is found to be 3.03 D, differing by 0.07 D from the average experimental value. It is interesting to consider the question of the possible rotation of the group $-\overset{\overset{O}{\|}}{C}-N(C_2H_5)_2$. There are indications in the literature that the group $-N(CH_3)_2$ belongs to the irregular type and may have free rotation at an angle of 74° [7]. The calculations we have carried out for N,N-diethyl(dialkoxyphosphinyl) formamides taking into account only the position of the $-\underset{\underset{\textstyle O}{\|}}{C}-N(C_2H_5)_2$- group (configurations A_1 and A_2) give a mean dipole moment of 3.73 D, which is 0.77 D greater than the experimentally found value. Configurations B_1 and B_2 present a second possible position of the $-\underset{\underset{\textstyle O}{\|}}{C}-N(C_2H_5)_2$- group and give a dipole moment of 2.31 D, which is 0.65 D less than the experimentally found value. If the two positions of the group $-\underset{\underset{\textstyle O}{\|}}{C}-N(C_2H_5)_2$ are considered to be equally probable, then the experimentally found value will differ from the calculated value by 0.07 D.



A_2 B_2

Fig. 4

EXPERIMENTAL

The dipole moments of N,N-diethyl(dialkoxyphosphinyl)formamides were determined in benzene solution at 25°. They were calculated according to the formula:

$$\mu = 0.0127\cdot 10^{-18}\sqrt{(P_T - P_E - P_A)\cdot 298},$$

where P_E is equal to MR_D and is calculated from the Lorentz-Lorenz formula, and P_A is estimated to have five per cent of the value of P_E.

The N,N-diethyl(dialkoxyphosphinyl)formamides were synthesized by Rizpolozhensky and were kindly made available to us for investigation. Before the determinations were made, the substances were purified by distillation (Table 2).

In the calculation of MR_D we used the following values for the refractions of the individual groups: CH_2 4.618; —O— 1.643; O 2.211; the refraction of quinquevalent P was taken as 4.27 units, and the refraction of N in doubly substituted amides was taken as 2.49 units [6].

$(C_2H_5O)_2-\underset{\underset{\textstyle O}{\|}}{P}OCN(C_2H_5)_2$

C_2	$_{12}$	d_{12}	P_{12}	P_2
0.002167	2.2991	0.8757	27.07	229.9
0.003578	2.3169	0.8764	27.39	238.9
0.005021	2.3351	0.8764	27.72	243.2
0.005905	2.3463	0.8767	28.58	245.9
0.007951	2.3689	0.8791	28.35	242.9
0.009614	2.3930	0.8791	28.73	244.8
0.0000	2.2725	0.8740	26.63	–

$P_T = 236.00$; $P_{A+E} = 59.27$; $P_{Or} = 176.73$;

$\mu = 2.91$ D

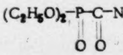
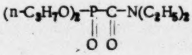
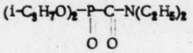
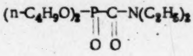
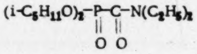
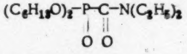
SUMMARY

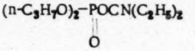
1. Dipole-moment measurements have been made on six N,N-diethyl(dialkoxyphosphinyl)formamides. The mean value obtained for the dipole moments is 2.96 D, which is close to the value calculated on the assumption of free rotation of the irregular groups (μ = 3.33 D).

2. Calculation of the interatomic distances between individual groups in N,N-diethyl(dialkoxyphosphinyl)formamides, taking into account the free rotation of the irregular groups, shows, however, the presence of a great measure of overlap of the spheres of action of Van der Waals forces due to methyl and methylene groups, and this makes it improbable that free rotation of the irregular groups can occur.

3. It is more probable that there is a synchronous vibration of OR and $-\underset{\underset{\textstyle O}{\|}}{C}N(C_2H_5)_2$ groups, having an amplitude of 180°.

TABLE 2

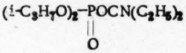
No.	Substance	B.p. °C	Pressure (mm Hg)	d_4^{25}	n_D^{25}	MR_D	
						found	calculated
1	 $(C_2H_5O)_2-\underset{\overset{\|}{O}}{P}-\underset{\overset{\|}{O}}{C}-N(C_2H_5)_2$	117-119	4	1.0806	1.4470	58.67	58.23
2	 $(n\text{-}C_3H_7O)_2-\underset{\overset{\|}{O}}{P}-\underset{\overset{\|}{O}}{C}-N(C_2H_5)_2$	131-132	2	1.0453	1.4478	67.91	67.47
3	 $(i\text{-}C_3H_7O)_2-\underset{\overset{|}{O}}{P}-\underset{\overset{|}{O}}{C}-N(C_2H_5)_2$	114-115	1.5	1.0339	1.4430	68.01	67.44
4	 $(n\text{-}C_4H_9O)_2-\underset{\overset{\|}{O}}{P}-\underset{\overset{\|}{O}}{C}-N(C_2H_5)_2$	148-149.5	2	1.0202	1.4480	76.98	76.70
5	 $(i\text{-}C_5H_{11}O)_2-\underset{\overset{\|}{O}}{P}-\underset{\overset{\|}{O}}{C}-N(C_2H_5)_2$	155-155.5	4	0.9963	1.4482	86.54	85.78
6	 $(C_6H_{13}O)_2-\underset{\overset{|}{O}}{P}-\underset{\overset{\|}{O}}{C}-N(C_2H_5)_2$	183-184.5	3.5	0.9707	1.4458	95.91	95.17


$(n\text{-}C_3H_7O)_2-PO\underset{\overset{\|}{O}}{C}N(C_2H_5)_2$

C_2	$_{12}$	d_{12}	P_{12}	P_2
0.001937	2.2978	0.8742	27.10	263.9
0.003404	2.3196	0.8750	27.51	278.9
0.004299	2.3314	0.8750	27.74	277.9
0.005082	2.3410	0.8757	27.89	272.0
0.007697	2.3765	0.8780	28.49	266.2
0.006839	2.3651	0.8764	28.35	273.2
0.0000	2.2725	0.8730	26.64	–

$P_T = 262.00$; $P_{A+E} = 72.02$; $P_{Or} = 189.98$;

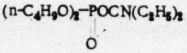
$\mu = 3.02$ D


$(i\text{-}C_3H_7O)_2-PO\underset{\overset{\|}{O}}{C}N(C_2H_5)_2$

C_2	$_{12}$	d_{12}	P_{12}	P_2
0.001907	2.2930	0.8747	27.01	238.5
0.004271	2.3200	0.8751	27.56	246.0
0.002972	2.3030	0.8750	27.22	231.0
0.005916	2.3408	0.8768	27.95	252.7
0.006579	2.3483	0.8767	28.11	253.8
0.008923	2.3764	0.8780	28.80	247.3
0.000	2.2725	0.8742	26.63	–

$P_T = 245.00$; $P_{A+E} = 72.14$; $P_{Or} = 172.86$;

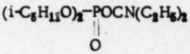
$\mu = 2.88$ D


$(n\text{-}C_4H_9O)_2-PO\underset{\overset{\|}{O}}{C}N(C_2H_5)_2$

C_2	$_{12}$	d_{12}	P_{12}	P_2
0.004052	2.3216	0.87555	27.58	263.7
0.001441	2.2898	0.8738	26.99	279.7
0.002404	2.3025	0.8740	27.24	279.3
0.005448	2.3310	0.8754	27.77	234.6
0.005908	2.3444	0.8760	28.04	265.1
0.007994	2.3733	0.8777	28.57	269.9
0.000	2.2725	0.8736	26.63	–

$P_T = 280.00$; $P_{A+E} = 81.64$; $P_{Or} = 198.36$;

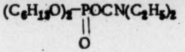
$\mu = 3.09$ D


$(i\text{-}C_5H_{11}O)_2-PO\underset{\overset{\|}{O}}{C}N(C_2H_5)_2$

C_2	$_{12}$	d_{12}	P_{12}	P_2
0.001847	2.2943	0.8742	27.07	267.5
0.002753	2.3035	0.8747	27.28	262.9
0.004602	2.3260	0.8751	27.80	270.0
0.005846	2.3393	0.8759	28.04	266.3
0.007085	2.3550	0.8772	28.06	567.2
0.000	2.2725	0.8735	26.63	–

$P_T = 270.00$; $P_{A+E} = 92.57$; $P_{Or} = 177.43$;

$\mu = 2.92$ D



$$(C_6H_{13}O)_2-\underset{\underset{O}{\|}}{P}OCN(C_2H_5)_2$$

C_2	$_{12}$	d_{12}	P_{12}	P_2
0.001489	2.2888	0.8735	27.02	282.3
0.004091	2.3198	0.8750	27.67	279.0
0.002480	2.3029	0.8740	27.30	298.0
0.003178	2.3106	0.8743	27.47	288.7
0.005001	2.3301	0.8750	27.91	279.2
0.005645	2.3391	0.8754	28.07	279.9
0.000	2.2725	0.8735	26.63	–

$$P_T = 282.00;\ P_{A+E} = 101.77;\ P_{Or} = 180.23;$$

$$\mu = 2.94\ D$$

Received June 23, 1952

A. M. Butlerov Research Institute of the
V. I. Ulyanov-Lenin Kazan State University

LITERATURE CITED

[1] B. A. Arbuzov and N. I. Rizpolozhensky, Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 5, 847 (1952).*

[2] A. E. Arbuzov and P. I. Rakov, Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 3, 237 (1950).

[3] H. Stuart, "The Structure of Molecules", United Sci. Tech. Press, 1937, p. 153.

[4] C. P. Smyth, G. L. Lewis, J. Am. Chem. Soc. 62, 1219, 1531 (1940).

[5] B. A. Arbuzov and T. G. Shavsha Proc. Acad. Sci. USSR, 79, No. 4, 599 (1951).

[6] K. Fuchs and Wolf, Hand. and Jahrbuch d. chem. Phys. 6, 365 (1938).

[7] I. R. Ruhoff, E. E. Reid, J. Am. Chem. Soc. 59, 401 (1937).

[8] T. G. Shavsha, Sci. Mem. Kazan State.Univ., 110, Book 9 (Chemistry), 1950.

---

* See Consultants Bureau translation, p. 755.

BLANK
PAGE

ESTERS OF ALKYLPHOSPHONIC ACIDS, AND THEIR PARACHORS

B. A. Arbuzov and V. S. Vinogradova

The principal methods for the preparation of alkylphosphonic esters are: action of alkyl halides on full phosphorous esters (the A. E. Arbuzov rearrangement), and action of alkyl halides on metal dialkyl phosphites. By these methods a considerable number of different alkylphosphonic esters have been obtained [1]. In our investigations of the parachors of organophosphorus compounds we have found it necessary to prepare alkylphosphonic esters of various types: 1) those having a long-chain hydrocarbon radical attached to phosphorus and short-chain hydrocarbon radicals in the ester groups, 2) those having a short-chain hydrocarbon radical attached to phosphorus, and long-chain hydrocarbon radicals in the ester groups, 3) those having long-chain hydrocarbon radicals in all three positions, and finally 4) those having unlike hydrocarbon radicals in the ester groups. The syntheses of alkylphosphonic esters of these types are described in the present communication.

A considerable number of esters of the first type are described in the literature [2]. In the experimental part of this paper the experimental part of this paper the results are given of the preparation of the diethyl esters of hexyl- and octyl-phosphonic acids by the rearrangement of triethyl phosphite under the action of the alkyl halide; the data given in the literature concerning these preparations are very incomplete [2].

As representatives of the second type we have synthesized esters of methylphosphonic acid. They were prepared both by the action of methyl iodide or dimethyl sulfate on trialkyl phosphites, and also, in certain cases, by the action of methyl iodide on sodium dialkyl phosphite. The constants of the esters obtained are given in Table 1.

Alkylphosphonic esters of the third type, having long hydrocarbon radicals, both attached to phosphorus and also in the ester groups, have not been described. Certain difficulties are met in their preparation. The synthesis of such esters by the action of an alkyl halide on a trialkyl phosphite does not proceed smoothly when the alkyl radicals are large [2]. When the reaction is carried out at moderate temperatures, it may not go to completion, and, owing to the closeness in boiling point of trialkyl phosphite and the isomeric dialkyl alkylphosphonate, their separation may not be complete.

When heating is carried out at high temperatures it is possible, as experiment shows, that decomposition will occur with splitting off of the corresponding olefin. For this reason we carried out parallel syntheses of these esters by the action of alkyl halides on sodium dialkyl phosphites. It must be pointed out that the preparation of substances having closely agreeing constants by the use of the two methods presents difficulty: owing to the high boiling point the use of a fractionating column gives rise to difficulty, and the value obtained for the boiling point of a high-boiling ester varies with design of the distilling flask, particularly with respect to the presence or absence of a small fractionating column when the boiling range is narrow. The constants of the esters obtained are given in Table 2.

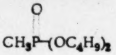
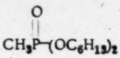
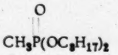
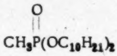
Mixed esters of alkylphosphonic acids have not been described in the literature. In order to prepare them we tried the partial transesterification of diethyl alkylphosphonates with the corresponding alcohols. We have previously used this method successfully both for the preparation of esters having identical radicals (trialkyl phosphites, dialkylphosphorous acids [3]), and also for the preparation of dialkylphosphorous acids having unlike alkyl radicals [4]. Experiment showed that transesterification of alkylphosphonic esters did not go in absence of catalysts, but catalysts of acid character, which gave results for trialkyl phosphites and dialkylphosphorous acids, did not give the desired result in the case of alkylphosphonic esters. Transesterification of alkylphosphonic esters occurs, though less readily than in the case of phosphorous esters, in presence of sodium. Using this method we have obtained for the first time the mixed alkylphosphonic esters given in Table 3.

A certain amount of the diester of the higher alcohol was obtained at the same time.

THE PARACHORS OF ALKYLPHOSPHONIC ESTERS

In previous investigations [5] we have examined the parachors of alkylphosphonic acids having radicals ranging from methyl to butyl on phosphorus and on oxygen, and we have found good agreement between the values found and those calculated assuming the following corrections for chain interaction: corrections for bending at the β-carbons of the ester chains and for parallelism of the ether chains beyond the β-carbon atom, and corrections (β, γ, δ) for the alkyl chain on the phosphorus, which are identical to the corrections for the alkyl chain in a carboxylic ester.

TABLE 1

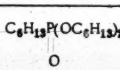
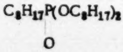
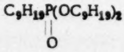
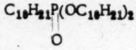
No.	Formula	B.p. (°C)	Pressure (mm Hg)	d_0^{20}	n_D^{20}	MR_D found	MR_D calculated	$\gamma 20$
1	 $CH_3\overset{O}{\overset{\Vert}{P}}(OC_4H_9)_2$	a) 111.0-111.5	5.5	0.9785	1.4240	54.32	54.68	28.2
		b) 105.5-106	5	0.9776	1.4235	54.26	54.68	28.1
2	 $CH_3\overset{O}{\overset{\Vert}{P}}(OC_6H_{13})_2$	a) 158-159.5	6.5	0.9432	1.4340	72.98	73.15	28.5
3	 $CH_3\overset{O}{\overset{\Vert}{P}}(OC_8H_{17})_2$	a) 200-200.5	5.5	0.9260	1.4405	91.30	91.62	28.9
4	 $CH_3\overset{O}{\overset{\Vert}{P}}(OC_{10}H_{21})_2$	a) 227.5-229	4.5	0.9117	1.4435	109.63	110.09	29.3
		b) 206-208.5	0.5	0.9094	1.4420	109.53	110.09	29.4

---

a) Prepared by the action of methyl iodide on the corresponding trialkyl phosphite.

b) Prepared by the action of methyl iodide or dimethyl sulfate on sodium dialkyl phosphite

TABLE 2

No.	Formula	B.p. (°C)	Pressure (mm Hg)	d_0^{20}	n_D^{20}	MR_D found	MR_D calculated	$\gamma 20$
1	 $C_6H_{13}\underset{O}{\underset{\Vert}{P}}(OC_6H_{13})_2$	a) 183.5-184.5	2.5	0.9205	1.4420	96.12	96.24	28.2
		b) 192.0-193.0	6.5	0.9215	1.4410	95.82	96.24	28.2
2	 $C_8H_{17}\underset{O}{\underset{\Vert}{P}}(OC_8H_{17})_2$	a) 234.5-235	3	0.9034	1.4450	123.37	123.95	28.95
		b) 236.5-237	3.5	0.9028	1.4477	124.0	123.95	29.0
3	 $C_9H_{19}\underset{O}{\underset{\Vert}{P}}(OC_9H_{19})_2$	a) 214.5-216	0.5	0.8904	1.4450	137.71	137.80	28.5
4	 $C_{10}H_{21}\underset{O}{\underset{\Vert}{P}}(OC_{10}H_{21})_2$	a) 241.5-243	0.5	0.8946	1.4510	151.30	151.66	29.7
		b) 230.5-231.5	0.07	0.8932	1.4522	151.93	151.66	29.6

---

a) Prepared via trialkyl phosphite.

b) Prepared via sodium dialkyl phosphite.

The question of the corrections for the interaction of the ether chains with the alkyl radical on the phosphorus has remained open owing to lack of evidence. Our syntheses of various alkylphosphonic esters may give the data required for the elucidation of these matters.

A study of the parachors of the ethyl esters of hexyl- and octyl-phosphonic acids confirmed our previous conclusions concerning the applicability of the corrections β, γ, and δ for the alkyl chain of carboxylic esters to the case of alkylphosphonic esters. In order not to introduce corrections for the alkyl group on the phosphorus, but to study only the interaction of the ester chains, we have determined the parachors of the methylphosphonic esters from dibutyl to didecyl.

TABLE 3

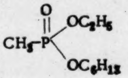
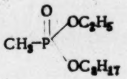
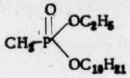
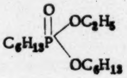
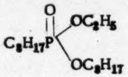
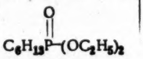
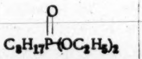
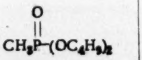
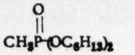
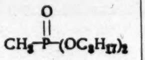
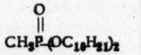
No.	Formula	B.p. (°C)	Pressure (mm Hg)	d_4^{20}	n_D^{20}	MR_D found	MR_D calculated	$\gamma 20$
1		119-120	8	0,9767	1,4260	54.61	54.68	–
2		134,0-135.0	7	0.9519	1.4312	64.26	63.92	–
3		151.0-152,0	4	0.9504	1.4335	72.37	73.15	–
4		162,5-163,5	9	0.9357	1.4350	77.62	77.77	28.3
5		192,5-194.0	4	0.9188	1.4412	96.16	96.24	28.8

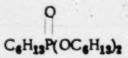
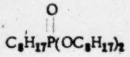
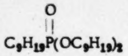
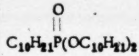
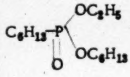
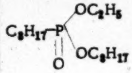
TABLE 4

No.	Formula	[P]found	[P]calcd.	Corrections	Discrepancy (%)	Notes
1	 $C_6H_{13}P(O)(OC_2H_5)_2$	530.0	532.5	2β(βγδ)	−0.5	–
2	 $C_8H_{17}P(O)(OC_2H_5)_2$	611.4	613.0	2β(βγδ)	−0.2	–
3	 $CH_3P(O)(OC_4H_9)_2$	490.8	492.4	2β, 2 ‖	−0.3	Prepared from dimethyl sulfate
	Ditto	490.3	492.4	2β, 2 ‖	−0.4	Prepared from CH_3I and the phosphite
4	 $CH_3P(O)(OC_6H_{13})_2$	647.8	649.1	2β, 4 ‖	−0.2	–
5	 $CH_3P(O)(OC_8H_{17})_2$	802.5	806.1	2β, 6 ‖	−0.4	–
6	 $CH_3P(O)(OC_{10}H_{21})_2$	964.8	963.8	2β, 8 ‖	+0.1	Prepared via the phosphite
	Ditto	961.5	963.8	2β, 8 ‖	−0.2	Prepared via sodium didecyl phosphite

The values of [P] (the parachor) found are in agreement with those calculated taking into account corrections for the parallelism of the ester chains beyond the β-carbon atom, as will be seen from the data in Table 4.

The parachors of alkylphosphonic esters can give interesting material concerning the presence of corrections for the interaction of the chains, but there are insufficient accurate data available at the present time for us to form a judgment concerning corrections in parachors of compounds of this type.

TABLE 5

No.	Formula	[P] found	[P] I calcd.	Corrections	Discrepancy (%)	[P] II calcd.	Corrections	Discrepancy (%)	[P] III calcd.	Corrections	Discrepancy (%)
1	 $C_6H_{13}P(O)(OC_6H_{13})_2$ a)	836.3	837.4	2β(βγδ) 8∥	−0.1	846.5	2β(βγδ) 4∥	−1.2	837.6	2β(βγδ) 8	−0.2
	Ditto b)	836.1	837.4	2β(βγδ) 8∥	−0.1	846.5	2β(βγδ) 4∥	−1.2	837.6	2β(βγδ) 8	−0.2
2	 $C_8H_{17}P(O)(OC_8H_{17})_2$ a)	1075.0	1067.6	2β(βγδ)14∥	+0.6	1095.7	2β(βγδ) 6∥	−0.9	1071.6	2β(βγδ)12	+0.3
	Ditto b)	1076.7	1067.6	2β(βγδ)14∥	+0.7	1095.7	2β(βγδ) 6∥	−0.9	1071.6	2β(βγδ)12	+0.4
3	 $C_9H_{19}P(O)(OC_9H_{19})_2$	1196.0	1182.9	2β(βγδ)17∥	+1.0	1205.6	2β(βγδ) 7∥	−0.8	1189.6	2β(βγδ)14	+0.5
4	 $C_{10}H_{21}P(O)(OC_{10}H_{21})_2$	1310.8	1298.8	2β(βγδ)20∥	+0.9	1325.8	2β(βγδ) 8∥	−1.1	1307.5	2β(βγδ)16	+0.2
5	 $C_6H_{13}P(O)(OC_2H_5)(OC_6H_{13})$	686.0	689.7	2β(βγδ) 2∥	−0.5	694.0	2β(βγδ)	−1.1	–	–	–
6	 $C_8H_{17}P(O)(OC_2H_5)(OC_8H_{17})$	843.7	844.3	2β(βγδ)4∥	−0.1	855.4	2β(βγδ)	−1.4	–	–	–

In the previous work on the parachors of alkyl phosphonic esters [5], we were unable to resolve the question of the possibility of interaction between all three alkyl chains when they are sufficiently long. The parachor results for didecyl decylphosphonate pointed to interaction between only the two ester chains, but this question cannot be finally settled on the basis of one example only. Also, the preparation of didecyl decylphosphonate by the isomerization of tridecyl phosphite was found to be capricious, and often the product of the isomerization of tridecyl phosphite was found to decompose with separation of decene, which dissolved in the distilled ester and modified its properties. It is evidently from this cause that the constants of the didecyl decylphosphonate previously described by us differ appreciably from those cited in the present communication.

The question of the interaction of chains in alkylphosphonic esters having long radicals on the phosphorus and in the ester groups can be resolved by the determination of the parachors of a series of esters. The values of the parachors obtained for the esters that we have synthesized are given in Table 5.

Under the heading [P] I (calcd.) are given the values of [P] calculated for interaction between all three chains — beyond the β-carbons of the ester chains and beyond the δ-carbon of the alkyl chain on the phosphorus; under [P] II (calcd) — for interaction of only the two ester chains; and under [P] III (calcd.) — for interaction of the two ester chains, but with doubled corrections for parallelism. It will be seen that the experimental values of [P] lie half way between the values calculated for the interaction of three chains ([P] I) and those calculated for interaction of the two ester chains ([P] II).

It is difficult to decide at present whether this departure of $[P]_{found}$ is to be explained by the difficulty of preparing these high-boiling esters in a sufficiently high degree of purity for accurate parachor determinations, or whether this nonagreement is to be explained by other causes, and the question of the parachor corrections for chain interaction in alkylphosphonic esters having long alkyl radicals on the phosphorus and in the ester groups remains an open one.

EXPERIMENTAL

Diethyl Methylphosphonate

a) Sodium diethyl phosphite was prepared from diethylphosphorous acid (i.e., the tautomeric mixture of diethyl hydrogen phosphite and diethyl phosphonate — Translator) (35 g) and sodium (6 g) in dry ether (250 ml). Methyl iodide (38 g) was added gradually under cooling (with water). Sodium iodide was not precipitated immediately, and when the addition of methyl iodide was complete the mixture was heated under reflux for 2 hrs 30 min. After separation of the sodium iodide (23 g) and removal of ether, vacuum distillation yielded diethyl methylphosphonate (20 g) of b.p. 80°/13 mm; n_D^{20} 1.4110; d_0^{20} 1.0548. A thick clear mass, soluble in water, remained behind in the flask.

b) Dimethyl sulfate (32 g) was added gradually under cooling to an ethereal solution of sodium diethyl phosphite prepared from diethylphosphorous acid (35 g) and sodium (6 g). Reaction was vigorous. When reaction was nearly complete the flask was heated on a water bath for 90 minutes. The precipitate was filtered off (31 g). The product obtained after removal of ether and distillation was diethyl methylphosphonate (34 g), b.p. 75-76°/10 mm, n_D^{20} 1.4092; d_0^{20} 1.0763. It is evident that the ester contained a small amount of dimethyl sulfate, which has a similar boiling point.

Dibutyl Methylphosphonate

a) A solution of sodium butoxide was prepared from sodium (5 g) and butyl alcohol, dibutylphosphorous acid (40 g) was added, and then dimethyl sulfate (26 g) was introduced slowly. Reaction was vigorous, and a voluminous precipitate formed, which did not settle on standing. A small amount of clear solution was obtained by centrifugation, and after removal of the alcohol and vacuum distillation it yielded dibutyl methylphosphonate (11 g) having the following constants: b.p. 105.5-106° at 5 mm, n_D^{20} 1.4235; d_0^{20} 0.9776; calculated MR_D 54.68; found MR_D 54.26; γ^{20} 28.1.

b) A mixture of tributyl phosphite (15 g) and methyl iodide (12 g, the theoretical amount is 8.6 g) was sealed in a tube. The tube was heated for four hours at 155-165° and for 2 hrs 30 min at 170-195°. Methyl iodide (4 g) and butyl iodide (10 g, b.p. 130°/755 mm) were distilled off, and vacuum distillation yielded dibutyl methylphosphonate (9 g, 72%) as a colorless liquid having the following constants: b.p. 111-111.5° at 5.5 mm; n_D^{20} 1.4240; d_0^{20} 0.9785; found MR_D 54.32; calculated MR_D 54.68; γ^{20} 28.2.

Found %: P 14.75
$C_9H_{21}O_3P$. Calculated %: P 14.88

Preparation of Dihexyl Methylphosphonate

A mixture of trihexyl phosphite (11.5 g) and methyl iodide [8 g (theory requires 4.8 g)] was sealed in a tube, which was then heated for four hours at 170-180°. Fractionation yielded methyl iodide (2 g), hexyl iodide (5 g), and a fraction of b.p. 156-180°/6 mm. The last was distilled from a flask having a small fused-on Widmer column [6] and yielded a fraction (4.5 g) having the following constants: b.p. 158-159.5° at 6.5 mm; d_0^{20} 0.9432; n_D^{20} 1.4340; found MR_D 72.98; calculated MR_D 73.15; γ^{20} 28.5.

Found %: P 11.78
$C_{13}H_{29}O_3P$. Calculated %: P 11.72

Preparation of Dioctyl Methylphosphonate

A mixture of trioctyl phosphite (17 g) and methyl iodide [10 g (theory requires 5.8 g)] was sealed in a tube, which was then heated for 3 hrs 30 min at 170-185°. Fractionation yielded methyl iodide (3.5 g), some octyl iodide, and dioctyl methylphosphonate (8 g) having the following constants: b.p. 200-200.5°/5.5 mm; d_0^{20} 0.9260; n_D^{20} 1.4405; found MR_D 91.30; calculated MR_D 91.62; γ^{20} 28.9

Found %: P 9.82
$C_{17}H_{37}O_3P$. Calculated %: P 9.76

Didecyl Methylphosphonate

a) A mixture of tridecyl phosphite (11.5 g) and methyl iodide [6 g(theory requires 3 g)] was sealed in a tube, which was then heated for four hours at 160-165° and for 3 hrs 30 min at 170-195°. Fractionation yielded methyl iodide (2.8 g), some decyl iodide of b.p. 118°/5.5 mm, and didecyl methylphosphonate (3.5 g) having the following constants: b.p. 227.5-229° at 4.5 mm; d_4^{20} 0.9117; n_D^{20} 1.4435; found MR_D 109.63; calculated MR_D 110.09; γ^{20} 29.3.

Found %: P 8.20
$C_{21}H_{45}O_3P$. Calculated %: P 8.23

The ester was a colorless oil.

b) Sodium didecyl phosphite was prepared in a medium of ligroin (b.p. 75-110°) from didecylphosphorous acid (21 g) and sodium (1.3 g). When the mixture was heated on the water bath, the sodium reacted vigorously. The reaction finally slowed down, and the sodium was floated off, extracted, and flattened out, after which it again reacted when the mixture was warmed. The amount of unchanged sodium was 0.2 g. Methyl iodide (9 g) was added, and sodium iodide was precipitated and was removed by centrifugation. The liquid frothed strongly when the ligroin was distilled off. Vacuum fractionation yielded a fraction of b.p. 198-213° /1 mm; a large amount of residue residue remained in the flask. In a second fractionation a didecyl methylphosphonate fraction was obtained (in negligible amount); it had the following constants: b.p. 206-208.5° at 0.5 mm; d_4^{20} 0.9094; n_D^{20} 1.4420; found MR_D 10 9.53; calculated MR_D 110.09; γ^{20} 29.4.

Found %: P 8.50
$C_{21}H_{45}O_3P$. Calculated %: P 8.23

Ethyl Hexyl Methylphosphonate

Diethyl methylphosphonate (20 g) and hexyl alcohol (20 g) were placed in a flask having a small fused-on Widmer fractionating column, and a small piece of sodium was added. At a bath temperature of 175-180° ethanol started to come over. After some time the distillation of alcohol slowed down considerably: more sodium was added, and distillation of alcohol started up again. The total amount of sodium added was 0.2 g, and the amount of alcohol distilled off was 5.5 ml. Fractionation yielded a small amount of low-boiling fractions, hexyl alcohol, and fractions having boiling points of 120-124°/9 mm and 155-160°/8 mm. A second distillation of the fraction of b.p. 120-124°/9 mm yielded ethyl hexyl methylphosphonate (9.5 g) having the following constants: b.p. 119-120° at 8 mm; d_4^{20}0.9767; n_D^{20} 1.4260; found MR_D 54.61; calculated MR_D 54.68.

Found %: P 14.47
$C_9H_{21}O_3P$. Calculated %: P 14.87.

A second distillation of the fraction of b.p. 155-160° yielded dihexyl methylphosphonate (3 g) having b.p. 158.5-160° at 8 mm; d_4^{20} 0.9441; n_D^{20} 1.4300.

Ethyl Octyl Methylphosphonate

Diethyl methylphosphonate (17 g), octyl alcohol (18 g), and a small piece of sodium (0.05-0.1 g) were placed in a flask having a Widmer fractionating column. Alcohol started to come over at a bath temperature of 190°; the bath was maintained at 205-210°, and was heated toward the end to 218°. In the course of four hours 6 ml of alcohol came over. Toward the end a small amount of white precipitate formed in the flask. Distillation yielded octyl alcohol (b.p. 65-130°/9 mm), a fraction (15 g) of b.p. 130-155°/10 mm, and a fraction of b.p. 175-177°/2 mm. In the redistillation of the fraction of b.p. 130-155°/10 mm, practically the whole came over a range of one degree, giving ethyl octyl methylphosphonate (6 g) having the constants: b.p. 134-135.5° at 7 mm; d_4^{20} 0.9519; n_D^{20} 1.4312; found MR_D 64.26; calculated MR_D 63.92.

Found %: P 12.77
$C_{11}H_{25}O_3P$. Calculated %: P 13.11

The fraction of b.p. 175-177°/2 mm was dioctyl methylphosphonate (3.5 g). After being redistilled it had b.p. 202-204°/7 mm; d_4^{20} 0.9269; n_D^{20} 1.4380.

Decyl Ethyl Methylphosphonate

Diethyl methylphosphonate (16 g) and decyl alcohol (20 g) were placed in a flask having a Widmer fractionating column, and sodium (0.05-0.1 g) was added. Alcohol began to come over at a bath temperature of 165°; the temperature was maintained at 215-220°, and, when distillation of alcohol was nearly complete, it was raised to 225°. In the course of four hours, 5.5 ml of alcohol came over; a small amount of white precipitate formed in the flask. The following fractions were obtained, on distillation:

Fraction I, b.p. 72-145°/9 mm
Fraction II, b.p.145-155°/5 mm
Fraction III, b.p.155-230°/5 mm

Redistillation of Fractions II and III yielded decyl ethyl methylphosphonate (10 g) having the constants: b.p. 151-152°/4 mm; n_D^{20} 1.4325; d_4^{20} 0.9504; found MR_D 72.37; calculated MR_D 73.15.

Found %: P 11.83

$C_{13}H_{29}O_3P$. Calculated %: P 11.72

From the high-boiling fractions didecyl methylphosphonate (4 g) was isolated; it had the following constants: b.p. 226.5-227.5 at 5 mm; n_D^{20} 1.4430; d_0^{20} 0.9177.

Ethyl Hexyl Hexylphosphonate

The diethyl hexylphosphonate required for the transesterification reaction was obtained by the action of hexyl bromide on triethyl phosphite [2]. The triethyl phosphite (20 g) and hexyl bromide (25 g) were placed in a flask having a small fractionating column, and the flask was heated in a bath of Wood's metal. Ethyl bromide began to come over at a bath temperature of 160°, and, towards the end of the distillation, the bath temperature was 200°. Distillation of the residue yielded hexyl bromide (6 g) and diethyl hexylphosphonate, which, after being redistilled twice, had the constants: b.p. 123.5-125.5/8.5 mm; d_0^{20} 0.9659; n_D^{20} 1.4295.

Transesterification of Diethyl Hexylphosphonate with Hexyl Alcohol

Transesterification does not proceed in absence of catalyst; neither phosphoric acid nor camphorsulfonic acid will act as a catalyst, but the reaction proceeds in presence of sodium. Diethyl hexyl phosphonate (12 g) and hexyl alcohol (15 g) were placed in a flask having a small fractionating column, and a small piece of sodium was added. Alcohol began to come over at a bath temperature of 180-190°; 3.5 ml came over. Vacuum distillation yielded hexyl alcohol, b.p. 62-65°/9 mm, and the fractions;

Fraction I, b.p. 125-137°/9 mm
Fraction II, b.p. 139-147°/8 mm
Fraction III, b.p.189-192°/8 mm

As a result of several refractionations of these fractions, ethyl hexyl hexylphosphonate (5 g) was obtained. It had the constants: b.p.162.5-163.5°/9 mm; d_0^{20} 0.9357; n_D^{20} 1.4350; found MR_D 77.62; calculated MR_D 77.77; γ^{20} 28.3.

Found %: P 11.04, 10.93

$C_{14}H_{31}O_3P$. Calculated %: P 11.1

In each refractionation, evidently owing to disproportionation, a further amount of fraction of b.p. 162.5-163.5°/9 mm was obtained.

Ethyl Octyl Octylphosphonate

The diethyl octylphosphonate required for the transesterification reaction was obtained by the action of octyl bromide (27 g) on triethyl phosphite (18.8 g) [2]. Ethyl bromide was driven off at a bath temperature of up to 200° (at the end of the reaction); 4.5 ml of ethyl bromide was driven off. Distillation yielded octyl bromide, b.p. 85-90°/11 mm and a fraction of b.p. 145-152°/10 mm. From the latter fraction there was obtained diethyl octylphosphonate (18 g) having the constants: b.p. 149.5-150.5°/10 mm; d_0^{20}0.9490; n_D^{20} 1.4335; γ^{20} 28.7

Diethyl octylphosphonate (13 g), octyl alcohol (17 g), and sodium (0.1 g) were placed in a flask having a small Widmer fractionating column. Ethyl alcohol began to distill at a bath temperature of 200°, and 2.5 ml came over in the course of five hours; toward the end the bath temperature was 215°. Distillation yielded octyl alcohol (11.5 g), a fraction of b.p. 85-185°/9 mm (2.5 g), and a fraction of b.p. 185-200°/4 mm; distillation was accompanied by considerable frothing.

By distillation of the higher fraction,ethyl octyl octylphosphonate was isolated in very small amount; it had the constants: b.p. 192.5-194° at 4 mm; d_0^{20}0.9188; n_D^{20} 1.4412; found MR_D 96.16; calculated MR_D 96.24; γ^{20} 28.8

Found %: P 9.30, 9.20

$C_{18}H_{39}O_3P$. Calculated %: P 9.26.

The ester is a viscous yellowish liquid.

Dihexyl Hexylphosphonate

a) Dihexyl hexylphosphonate was obtained by the A.E.Arbuzov isomerization of trihexyl phosphite (b.p.171-173°/5 mm) in presence of hexyl bromide (b.p. 47.5-48°/15 mm). Trihexyl phosphite (7 g) was heated with hexyl bromide (1.5 g) in a flask fitted with an air condenser for seven hours, the bath temperature being 160-200°. In the course of vacuum distillation, first hexyl bromide came over, then a certain amount of decomposition occurred, and finally dihexyl hexylphosphonate came over; it had b.p. 183.5-184.5°/2.5 mm; n_D^{20} 1.4420; d_0^{20} 0.9205; found MR_D 96.12; calculated MR_D 96.24; γ^{20} 28.2.

Found %: P 9.32, 9.13

$C_{18}H_{39}O_3P$. Calculated %: P 9.24

b) Dihexylphosphorous acid was obtained by the action of PCl_3 (14 g) on hexyl alcohol (31 g) under cooling with snow. Hydrogen chloride was removed by suction. Distillation yielded hexyl chloride (8 g; b.p. 134-135°) and dihexylphosphorous acid (19 g, 76%), b.p. 153-155°/6 mm, n_D^{20} 1.4340.

A solution of sodium dihexyl phosphite was obtained from dihexylphosphorous acid of b.p. 153-155°/6 mm (19 g), sodium (1.7 g), and benzene (100 ml); the sodium was consumed completely in a three-hour heating on the water bath. Hexyl bromide (13 g; b.p. 66°/34 mm) was added gradually to the solution obtained, and the flask was again heated for 3 hours 30 min. The colloidal precipitate of sodium bromide that formed during the reaction was washed out by shaking the mass carefully with water in a separating funnel; this operation was repeated. The benzene solution obtained was dried with calcium chloride, the benzene was distilled off, and the residue was vacuum-distilled. A small amount of hexyl bromide was obtained, and a fraction of b.p. 178-180°/2 mm was isolated. There was a thick residual mass of sodium dihexyl phosphite. Redistillation yielded a substance of b.p. 192-193°/6.5 mm; n_D^{20} 1.4410; d_0^{20} 0.9215; found MR_D 95.82; calculated MR_D 96.24; γ^{20} 28.2.

Found %: P 8.90, 9.23

$C_{18}H_{39}O_3P$. Calculated %: P 9.24

Dioctyl Octylphosphonate

Dioctyl octylphosphonate was prepared by two methods:

a) It was prepared, analogously to dihexyl hexylphosphonate, by isomerization of trioctyl phosphite (16 g; b.p. 212-214°/2 mm) in presence of octyl bromide (2.5 g; b.p. 196-197.5°). The mixture was heated for 12 hours, the bath temperature being 160-200°. Toward the end a yellowish coloration occurred in the liquid. In the vacuum distillation, first octyl bromide came over, then, when distillation of the ester began, considerable decomposition occurred, after which the following fractions were obtained:

Fraction I, b.p. 223-227°/3 mm
Fraction II, b.p. 234.5-236.5°/3.5-4 mm

Redistillation yielded the ester, which had b.p. 234.5-235°/3 mm; n_D^{20} 1.4450; d_0^{20} 0.9034; found MR_D 123.37; calculated MR_D 123.95; γ^{20} 28.9.

Found %: P 7.39, 7.35

$C_{24}H_{51}O_3P$. Calculated %: P 7.40

b) A solution of sodium dioctyl phosphite was obtained from dioctylphosphorous acid (14.5 g) (which was obtained by transesterification of diethylphosphorous acid), sodium (1.0 g), and benzene (150 ml); octyl bromide (9 g) was added to this solution in portions. Reaction was completed by heating the mixture on a water bath for 3 hours. The sodium bromide formed did not settle; it was precipitated by adding water (0.5 ml) and centrifuging. The benzene solution was dried with calcium chloride, and the benzene was driven off. As a result of three distillations, dioctyl octylphosphonate (7 g) was obtained; it had the constants: b.p. 236.5-237° at 3 mm; d_0^{20} 0.9028; n_D^{20} 1.4477; found MR_D 124.0; calculated MR_D 123.95; γ^{20} 29.0.

Found %: P 7.69

$C_{24}H_{51}O_3P$. Calculated %: P 7.40

Dinonyl Nonylphosphonate

This was prepared by isomerization of trinonyl phosphite of b.p. 186.5-188°/0.018 mm (9 g) in presence of nonyl bromide of b.p. 80-81°/5.5 mm (2 g). Heating was for 7 hours at a bath temperature of 160-200°; the liquid in the flask became somewhat yellow. Nonyl bromide was distilled off, and after slight decomposition the ester followed (b.p. 214.5-216°/0.5 mm), leaving negligible residue; it had constants: n_D^{20} 1.4450; d_0^{20} 0,8904; found MR_D 137.71; calculated MR_D 137.80; γ^{20} 28.5.

Found %: P 6.60; 6.64. $C_{27}H_{57}O_3P$. Calculated %: P 6.73.

Didecyl Decylphosphonate

a) The ester was obtained by the isomerization reaction: tridecyl phosphite of b.p. 250-252°/(uncorrected) 2.5 mm (13 g) was heated with decyl bromide of b.p. 122-123°/18 mm (3 g) for 16 hours at a bath temperature of 160-200°; the material yellowed strongly. After a small amount of decyl bromide had been distilled off, there was some considerable decomposition; some distillate was obtained by use of the mercury pump: b.p. 241.5-243°/0.5 mm (it was not found possible to obtain a greater rarefication in the distillation). Finally, considerable decomposition set in; a residue remained in the flask. The constants of the ester obtained were: n_D^{20} 1.4510; d_0^{20} 0.8946; found MR_D 151.30; calculated MR_D 151.66; γ^{20} 29.7.

Found %: P 6.56, 6.48

$C_{30}H_{63}O_3P$. Calculated %: P 6.16

b) Didecylphosphorous acid was obtained by the action of phosphorus trichloride on decyl alcohol. The phosphorus trichloride was added dropwise to the decyl alcohol (24 g), and hydrogen chloride was drawn off under suction at room temperature. Distillation yielded decyl chloride of b.p. 67-69°/9 mm (8 g) and didecylphosphorous acid of b.p. 188-194°/0.5 mm (15 g, 85%).

Action of decyl bromide on sodium didecyl phosphite. A solution of sodium didecyl phosphite was prepared from didecylphosphorous acid (14 g), sodium (0.9 g), and benzene (100 ml), and decyl bromide (8.7 g) was added. No sodium bromide came down. The mixture was heated under reflux for 5 hours: there was much frothing, but it gradually subsided. The emulsion formed did not readily settle out; ether and sodium chloride were added. The ether–benzene solution was dried with calcium chloride, and the ether and benzene were driven off. Distillation yielded didecyl decylphosphonate, b.p. 234-235°/0.8 mm (11 g). After being redistilled, the ester had the constants: b.p. 230.5-231.5°/0.07 mm; d_0^{20}0.8932; n_D^{20} 1.4522; found MR_D 151.93; calculated MR_D 151.66; γ^{20}29.6.

SUMMARY

1. The following alkylphosphonic esters have been synthesized: dibutyl, dihexyl, dioctyl, and didecyl methylphosphonates; dihexyl hexylphosphonate, dioctyl octylphosphonate, dinonyl nonylphosphonate, and didecyl decylphosphonate.

2. Mixed esters of alkylphosphonic acids have been obtained for the first time by a transesterification reaction: ethyl hexyl, ethyl octyl, and ethyl decyl methylphosphonates; ethyl hexyl hexylphosphonate; and ethyl octyl octylphosphonate.

3. The parachors of the alkylphosphonic esters have been determined, and conclusions have been reached concerning the corrections for chain interaction.

A.M.Butlerov Chemical Research Institute
of the V.I. Ulyanov-Lenin Kazan State University

Received June 23,1952

LITERATURE CITED

[1] V.Plets. Organic Compounds of Phosphorus, Defence Industry Press, 1940; G. Kosolapoff. Organophosphorus Compounds, 121-125 and 148-151.

[2] A.H.Ford-Moore, and J.H.Williams. J.Chem.Soc., 1465 (1947); G.Kosolapoff. J.Am.Chem.Soc., 67, 1180 (1945).

[3] B.A.Arbuzov and V.S.Vinogradova. Bull.Acad.Sci.USSR, Div.Chem.Sci., 733 (1951); V.S.Vinogradova. Sci. Mem. Kazan Univ. 110, Book 9, 67 (1950).

[4] B.A.Arbuzov and V.S.Vinogradova. Proc.Acad.Sci.USSR, 83, 79 (1952); G.Kosolapoff. J.Am.Chem.Soc., 73, 49, 89 (1951).

[5] B.A.Arbuzov and V.S.Vinogradova. Bull.Acad.Sci.USSR., Div.Chem.Sci., 459 (1947); V.S.Vinogradova. Sci. Mem. Kazan Univ., 110, Book 9, 24 (1950).

[6] K.Bernkhauer. Introduction to Laboratory Technique in Organic Chemistry, United Sci.Tech.Press, p. 72 (1935).

BLANK
PAGE

CERTAIN ALKYLPHOSPHONOTHIONIC, ALKYLPHOSPHONOSELENONIC, DIALKYLPHOSPHINIC, AND ALKYLPHOSPHONOUS ESTERS, AND THE MECHANISM OF ADDITION TO ALKYLPHOSPHONOUS ESTERS

A. I. Razumov, O. A. Mukhacheva, and Sim-Do-Khen

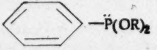
We have been concerned in recent years with the study of certain peculiar properties of various derivatives of alkylphosphonic acids, and have obtained rather interesting results. It was desirable to extend the work to the corresponding properties of the thio analogs of these compounds, in particular alkylphosphonothionic esters, which can be prepared by addition of sulfur to alkylphosphonous esters, $RP(OR)_2$. It was to be expected that addition of sulfur to such esters would proceed fairly readily. A. E. Arbuzov has pointed out in one of his papers [1] that replacement of OR by R in esters of the type $P(OR)_3$ should lead to an increase in the readiness with which addition reactions occur, and also in the readiness with which isomerization (or rearrangement) reactions occur, since these latter reactions proceed the more readily (other things being equal), the greater the tendency for addition to occur.

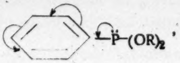
A. E. Arbuzov established a clearly defined parallelism between the rates of sulfur addition to certain tervalent phosphorus compounds and isomerization reactions. Hence, it was to be expected that not only would the ease of sulfur addition be greater for alkylphosphonous esters than for esters of the type $P(OR)_3$, but also the rate of isomerization would be greater. Actually, as will be seen later, the alkylphosphonous esters that we have synthesized have an extremely high tendency to undergo addition reactions and show a greater readiness to undergo isomerization than esters of the types $P(OR)_3$ and $ArP(OR)_2$. At the same time, A. E. Arbuzov remarks in his paper that the question of the cause of the increase in isomerization rate in the phosphorous ester series remains an open one. We consider that the tendency to undergo addition, and hence also, to a certain extent, isomerization, can be explained as follows. Addition reactions at tervalent P are obviously dependent on the presence there of an unshared pair of electrons and also on the nature of the substituents on the phosphorus atom. When the inductive effect of the substituent becomes more negative, or less positive, the tervalent phosphorus compound will become less inclined to undergo addition reactions. Hence the tendency of tervalent P to undergo addition reactions should diminish along the series:

$$R_3P > R_2P(OR) > RP(OR)_2 > P(OR)_3,$$

where R is an aliphatic radical.

On the other hand, the presence of a coordinately unsaturated atom having multiple bonds adjacent to the tervalent P must reduce the tendency for addition to occur at the phosphorus atom. Thus, in the compound



a displacement of electrons is possible , and consequently arylphosphonous esters should have a lower tendency to undergo addition than the corresponding alkylphosphonous esters, other things being equal: $RP(OR)_2 > ArP(OR)_2$.

Actually, comparative observations on the alkylphosphonous esters that we have synthesized indicate that they undergo addition reactions with sulfur and halogens and undergo the isomerization reaction considerably more readily than esters of the types $P(OR)_3$ and $ArP(OR)_2$. Thus, A. E. Arbuzov brought about addition of bromine to the ester $P(OC_4H_9)_3$-i by slow addition of dry bromine at ordinary temperature. However, for the ester $C_4H_9P(OC_4H_9)_2$-i, for example, the analogous reaction is difficult to carry out at ordinary temperature, and usually considerable cooling (to -15° or -20°) is necessary in order to preserve the reaction products. A.E. Arbuzov generally carried out addition of sulfur to esters of the type $P(OR)_3$ in carbon disulfide solution. For esters of the type $RP(OR)_2$, we used benzene as solvent, but sulfur, and also selenium, readily added also in absence of solvent, in both cases with considerable evolution of heat. A similar situation is found for the isomerization reaction. The esters $C_2H_5P(OC_2H_5)_2$ and $C_4H_9P(OC_4H_9)_2$-i isomerize considerably more readily and rapidly than the corresponding phosphorous esters. Thus, A.E. Arbuzov has shown that five hours' heating at 160° is required for the isomerization of the ester $P(OC_4H_9)_3$-i, whereas isomerization of the ester $C_4H_9P(OC_4H_9)_2$-i requires only three hours at 100°, other conditions being the same.

As would be expected, the ester $C_2H_5P(OC_2H_5)_2$ isomerizes still more readily; two hours at 70° is sufficient. These experiments confirm the explanation given above of the causes of the higher rates of addition reactions for compounds of the type $RP(OR)_2$, as compared with those of the type $P(OR)_3$.

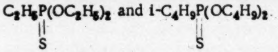
Alkylphosphonous esters were prepared from the corresponding alkylphosphonous dichlorides [2,3] in yields of up to 85% by the action of the corresponding alcohol in presence of a base:

$$RPCl_2 + 2ROH + 2C_5H_5N \longrightarrow RP(OR)_2 + 2C_5H_5N\cdot HCl.$$

Aliphatic esters of alkylphosphonous acids have not been described in the literature and so present interest on their own account. Also, they may be used as starting materials for the preparation of the required alkylphosphonothionic esters. The following esters were prepared:

$$C_2H_5P(OC_2H_5)_2 \text{ and } i\text{-}C_4H_9P(OC_4H_9)_2.$$

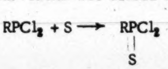
These are mobile liquids of characteristic, unpleasant odor which combine vigorously with the oxygen of the air. By taking advantage of the tendency, already discussed, of esters of the type $RP(OR)_2$ to undergo addition reactions, we obtained the desired alkylphosphonothionic esters (addition of sulfur):



$$C_2H_5\underset{\underset{S}{\|}}{P}(OC_2H_5)_2 \text{ and } i\text{-}C_4H_9\underset{\underset{S}{\|}}{P}(OC_4H_9)_2.$$

The yields obtained of these esters were almost quantitative. They are colorless liquids of rather pleasant odor. Only one ester of this type appears in the literature: $i\text{-}C_5H_{11}\underset{\underset{S}{\|}}{P}(OC_2H_5)_2$, described in the last century by Guichard [4]. Hydrolysis of the alkylphosphonothionic esters gave the corresponding acids as paraffinlike products; our study of these is not complete.

In the method described for the preparation of alkylphosphonothionic esters, it will be seen that alkylphosphonous esters are required as starting materials. These substances are difficult to work with, for they react very readily with the oxygen of the air. In order to avoid this stage in the preparation of the esters, we have tried also another method for their preparation: sulfur was caused to add directly to an alkylphosphonous dichloride:



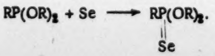
$$RPCl_2 + S \longrightarrow \underset{\underset{S}{|}}{RPCl_2}$$

and chlorine was then replaced by alkoxy either by the action of alkoxide or by treatment with the alcohol in presence of a tertiary base.

The addition of sulfur to an alkylphosphonous dichloride has been effected previously by Guichard [4]: he heated these substances together in a sealed tube at 125°. He gave no indication of the yields. We have brought about the reaction much more readily by heating the alkylphosphonous dichloride with sulfur in a flask fitted with reflux condenser for one hour in presence of a catalyst ($AlCl_3$). The yields were almost quantitative.

Replacement of chlorine in the alkylphosphonothionic dichloride by the alkoxy group is preferably carried out by the action of the alkoxide, for by the action of the alcohol products of unpleasant odor are obtained and an additional wash with water is necessary (they then show a slight acid reaction, but do not differ appreciably in their constants from the esters prepared by the other method).

Selenium combines with alkylphosphonous esters with equal ease, an appreciable amount of heat being evolved; in this way we prepared esters of alkylphosphonoselenonic acids, which have not been described previously. We used "metallic" selenium that had been ground to a powder, and this combined with the esters both in a solvent, and in absence of solvent, according to the equation:

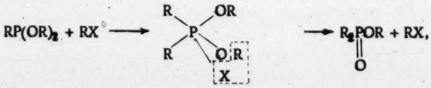


$$RP(OR)_2 + Se \longrightarrow R\underset{\underset{Se}{\|}}{P}(OR)_2.$$

The isomerization of alkylphosphonous esters proceeds very readily, as stated above; the reaction follows the Arbuzov scheme:

TABLE

No.	Formula	B.p. (°C)	Pressure (mm Hg)	d_4^{20}	n_D^{20}	MR_D		Yield %
						found	calculated	
1	$i\text{-}C_4H_9PCl_2$	48.5-49	12	1.1720	1.4719	38.54	38.15	26
2	$C_2H_5\underset{\underset{S}{\|}}{P}Cl_2$	82.5	45.5	1.3550	1.5413	–	–	80
3	$C_2H_5P(OC_2H_5)_2$	137-139	760	0.9064	1.4222	42.0	41.33	60
4	$i\text{-}C_4H_9P(OC_4H_9\text{-}i)_2$	105.5-107.5	12.5	0.8677	1.4290	69.20	69.04	85
5	$C_2H_5\underset{\underset{S}{\|}}{P}(OC_2H_5)_2$	86.5-87	12	1.0349	1.4617	–	–	80
6	$i\text{-}C_4H_9\underset{\underset{S}{\|}}{P}(OC_4H_9\text{-}i)_2$	135.5-136	12	0.9636	1.4420	–	–	Quantitative
7	$C_2H_5\underset{\underset{Se}{\|}}{P}(OC_2H_5)_2$	97.5	11	1.2743	1.4872	–	–	75
8	$i\text{-}C_4H_9\underset{\underset{Se}{\|}}{P}(OC_4H_9\text{-}i)_2$	144-146	14	1.084	1.4571	–	–	90
9	$(C_2H_5)_2\underset{\underset{O}{\|}}{P}OC_2H_5$	91-92	14	0.9964	1.4301	38.89	39.13	65
10	$(i\text{-}C_4H_9)_2\underset{\underset{O}{\|}}{P}OC_4H_9\text{-}i$	99-102	3	0.9151	1.4311	66.21	66.47	80
11	$(C_2H_5)_2\underset{\underset{O}{\|}}{P}Cl$	108-109.5	16	1.1394	1.4647	34.07	33.59	70
12	$C_2H_5\underset{\underset{S}{\|}}{P}(OH)_2$	Paraffinlike substance	–	–	–	–	–	–
13	$i\text{-}C_4H_9\underset{\underset{S}{\|}}{P}(OH)_2$	Ditto	–	–	–	–	–	–
14	$C_2H_5\underset{\underset{O}{\|}}{P}OH$	″	–	–	–	–	–	–
15	$(i\text{-}C_4H_9)_2\underset{\underset{O}{\|}}{P}OH$	″	–	–	–	–	–	–



In this way we prepared dialkylphosphinic esters that have not been described previously.

Dialkylphosphinic esters readily react with phosphorus pentachloride with formation of dialkylphosphinic chlorides: $R_2\underset{\underset{O}{\|}}{P}Cl$.

Hydrolysis of the dialkylphosphinic esters yielded the corresponding acids as paraffinlike products, the study of which has not been completed. One of these acids $(i\text{-}C_4H_9)_2POH$ is described in the literature [5] as an oily liquid.

The substances that we have synthesized are given with their constants in the table.

Note. The atomic refraction of P in alkylphosphonous derivatives is taken to be 7.04.

EXPERIMENTAL

1. Synthesis of Diethyl Ethylphosphonite. The materials taken for reaction were: ethylphosphonous dichloride (50 g), ethanol (35 g), and pyridine (60 g). The same experimental conditions were used as in the preparation of the isobutyl compound [2]. The yield of pure product was 34 g (60%), and it had b.p. 137-139°; d_0^{20} 0.9064; n_D^{20} 1.4222; found MR_D 42.0; calculated MR_D 41.33: This ester is a colorless liquid of unpleasant odor. It combines very readily with the oxygen of the air – much more readily than its isobutyl homolog. It is readily soluble in benzene and ether, and in a number of other organic solvents.

Found %: P 20.24; 20.38

$C_6H_{15}PO_2$. Calculated %: P 20.66

2. Addition of Bromine to Diethyl Ethylphosphonite. The ester (1.1 g) was placed in a test tube cooled with snow and salt, and carbon dioxide was passed continuously. Bromine was then added until a slight yellow color persisted (1.09 g of bromine; theory requires 1.17 g). Cuprous bromide gives a crystalline compound with diethyl ethylphosphonite.

3. Synthesis of Diethyl Ethylphosphonothionate. Diethyl ethylphosphonite(24.4 g) was placed in a flask fitted with reflux condenser and stirrer. Five times this amount of dry benzene was added, and a stream of carbon dioxide was passed. Sulfur (5.2 g) was then added in small portions at a time, the temperature of the mixture being regulated by the rate of sulfur addition so that it did not exceed 60°. The benzene was driven off, and the product was fractionally distilled. The ester (9.7 g, 64.5%; b.p. 86.5-87°/12 mm; d_0^{20} 1.0349; n_D^{20} 1.4617) is a colorless liquid that fumes in air and has a pleasant, refreshing odor. It is only slightly soluble in water.

Found %: S 17.79; 17.64

$C_6H_{15}O_2PS$. Calculated %: S 17.58.

Hydrolysis of the ester, and also of the corresponding phosphonothionic dichloride, yielded the acid – a paraffinlike substance.

4. Synthesis of Ethyl Diethylphosphinate. Diethyl ethylphosphonite (15 g) and ethyl iodide (15.5 g) were heated together in a sealed tube at 70°, heating being interrupted every hour in order to enable any change in the volume of liquid to be noted. After two hours the volume did not change further. Ethyl iodide was driven off, and the residue was vacuum-distilled, yielding a colorless liquid (9.7 g, 64.5%) having a pleasant but faint odor. It had b.p. 91-92°/14 mm, d_0^{20} 0.9964; n_D^{20} 1.4301; MR_D 38.89, calculated MR_D 39.13.

Found %: P 20.28; 20.72

$C_6H_{15}O_2P$. Calculated %: P 20.66

5. Addition of Sulfur to Ethylphosphonous Dichloride. Ethylphosphonous dichloride (22 g) was introduced into a three-necked flask fitted with reflux condenser, stirrer, and a tube, through which either carbon dioxide or nitrogen was passed. The temperature was measured by a thermometer that was immersed in the liquid. Sulfur (5.5 g) was added (in one lot), and the reaction mixture was brought to the boil (112°). Stirring was continued until all the sulfur had dissolved. Heating was then discontinued, stirring was stopped, and a mixture of aluminum chloride (0.6 g) and sulfur (0.2 g) was added rapidly. A violent reaction set in, and the temperature rose to 150°. The mass was heated further for two hours, and the final temperature was 172° (it did not rise above this value). The product was vacuum-distilled, yielding a colorless liquid having a pungent odor (22 g 80%). It had a b.p. 82.5°/45.5 mm, d_0^{20} 1.3550; n_D^{20} 1.5413. It did not react with water at room temperature, but remained as an oil at the bottom of the flask. The literature [2] gives 80-82°b.p.50 mm; d_0^{20} 1.36.

Found %: S 20.19; 20.06

$C_2H_5PSCl_2$. Calculated %: S 19.63.

6. Synthesis of Diethyl Ethylphosphonothionate via the Phosphonothionic Chloride. The ester was prepared from the phosphonothionic chloride (30 g), alcohol (17 g), and pyridine (29 g) in xylene; it was prepared also in alcoholic solution by the action of the alkoxide. The reaction was carried out in both cases in a three-necked flask fitted with stirrer and reflux condenser. The first method is the less satisfactory, for it yields an ester that has an unpleasant smell, even after it has been washed with water; also, a higher temperature is required. The ester obtained has a slightly acid character, which is not found when the ester is prepared by the action of the alkoxide or by addition of sulfur to diethyl ethylphosphonite.

7. Synthesis of Diethyl Ethylphosphonoselenonate. Diethyl ethylphosphonite (15 g) and "metallic" selenium (7.9 g) were introduced into a round-bottomed flask fitted with stirrer and reflux condenser. The selenium

added rapidly, and the temperature rose from 19° to 85°. The product was vacuum-distilled, yielding a product (17 g, 75%) of b.p. 97.5°/11.5 mm, d_0^{20} 1.2743; n_D^2 1.4872.

Found %: Se 34.20; 33.82
$C_6H_{15}O_2PSe$. Calculated %: Se 37.49

Diethyl ethylphosphonoselenonate is a colorless liquid having a feeble but characteristic odor.

8. Synthesis of Diethylphosphinic Chloride. A solution of ethyl diethylphosphinate (27 g) in carbon tetrachloride (54 g) was placed in a three-necked flask fitted with stirrer, reflux condenser, and thermometer. Phosphorus pentachloride was added slowly to the ester at 30°; toward the end, the temperature was raised to 60°. The solvent and the phosphoryl chloride formed were driven off under somewhat reduced pressure, and the acid chloride was then distilled over (17 g, 70%); it had b.p. 108-109.5/16 mm, d_0^{20} 1.1394; n_D^{20} 1.4647; found MR_D 34.07; calculated MR_D 33.59.

Found %: Cl 25.40; 25.54
$C_4H_{10}OPCl$. Calculated %: Cl 25.27

9. Synthesis of Isobutylphosphonous Dichloride. No description of isobutylphosphonous dichloride has appeared in the literature. We synthesized it from magnesium (18.22 g), cadmium iodide (110 g), isobutyl bromide (113 g), and phosphorus trichloride (130 g). The yield of analytically pure substance was 30 g (26%). It is a colorless liquid having a characteristic odor that is less powerful than that of the ethyl homolog. It has b.p. 48.5-49° or 12 mm; d_0^{20} 1.172; n_D^{20} 1.4719; found MR_D 38.54; calculated MR_D 38.15.

Found %: Cl 43.75; 43.52
$C_4H_9PCl_2$. Calculated %: Cl 44.20

10. Synthesis of Diisobutyl Isobutylphosphonite. Isobutyl alcohol (28 g) and pyridine (30 g) were dissolved in dry ether and introduced into a round-bottomed three-necked flask fitted with reflux condenser and stirrer. Slight cooling was applied, and isobutylphosphonous dichloride (30 g) was added gradually. The pyridine hydrochloride formed was filtered off, and the ether was driven off. The residue was vacuum-distilled, yielding a colorless liquid (36 g, 85%) having a characteristic odor, reminiscent of that of phosphorous esters. It had b.p. 105.5-107.5° at 12.5 mm, d_0^{20} 0.8677; n_D^{20} 1.4290; found MR_D 69.20; calculated MR_D 69.60.

Found %: P 13.24; 13.38
$C_{12}H_{27}PO_2$. Calculated %: P 13.28

11. Addition of Bromine to Diisobutyl Isobutylphosphonite. The ester (1.021 g) was placed in a test tube cooled to -15°; carbon dioxide was passed into it continuously in order to avoid reaction with oxygen. Bromine was added slowly until the liquid remained slightly yellow in color; 0.7 g was required (0.7 g is the calculated amount). The addition went quantitatively with evolution of much heat.

12. Addition of Cuprous Bromide to Diisobutyl Isobutylphosphonite. Cuprous bromide (0.57 g) was added to the ester (0.94 g), and the temperature rose from 17° to 60°. A colorless syrup was formed, and it was not found possible to isolate a crystalline product.

13. Synthesis of Diisobutyl Isobutylphosphonothionate. The ester was prepared by addition of sulfur to diisobutyl isobutylphosphonite. The latter (5 g) was dissolved in dry benzene in a flask fitted with reflux condenser, and the calculated amount of sulfur was added. The temperature rose from 18° to 90°. Benzene was driven off, and the residue was vacuum-distilled. The yield was quantitative. The ester is a colorless liquid of a pleasant but feeble odor. It has b.p. 135-136.5° or 12 mm; d_0^0 0.9865; d_0^{20} 0.9636; n_D^{20} 1.4480.

Found %: S 11.90, 11.84
$C_{12}H_{27}O_2PS$. Calculated %: S 12.0

Some (3 g) of the ester was hydrolyzed by boiling it with concentrated hydrochloric acid in a flask fitted with reflux condenser. The acid obtained is a paraffin-like substance, and its study is not yet complete.

14. Synthesis of Diisobutyl Isobutylphosphonoselenonate. Diisobutyl isobutylphosphonite (9 g) was introduced into a flask fitted with reflux condenser. Powdered "metallic" selenium (3 g) was added (in absence of solvent), and the temperature rose from 18° to almost 80°. The product was heated further on the water bath for one hour and was then vacuum-distilled, yielding a colorless liquid (11 g, i.e., higher than 90%) of characteristic odor having b.p. 144-146° at 14 mm; d_0^{20} 1.084; n_D^{20} 1.4571. Yield 11 g (about 90% of theory).

Found %: Se 24.80; 24.90

$C_{12}H_{27}O_2PSe$. Calculated %: Se 25.20

15. Synthesis of Isobutyl Diisobutylphosphinate. A mixture of diisobutyl isobutylphosphonite (12 g) and isobutyl iodide (9 g) was heated in a sealed tube for three hours at 100°, heating being interrupted every hour in order to enable any change in the volume of the liquid to be noted. After three hours the volume of the contents of the tube did not change further. The product was vacuum-distilled yielding a colorless liquid (9.5 g, 80%) having a faint characteristic odor. The ester is insoluble in water, but soluble in ether. It has b.p. 99-102° at 2 mm; d_4^{21} 0.9151; n_D^{21} 1.4311; found MR_D 66.21; calculated MR_D 66.47.

Found %: P 13.41; 13.25

$C_{12}H_{27}PO_2$. Calculated %: P 13.28.

Some (4.5 g) of the ester obtained was hydrolyzed with concentrated hydrochloric acid in a sealed tube at 150-160° for three hours. When the tube was opened, there was an odor of isobutene. Hydrogen chloride was evaporated off in a dish, and the acid remained as a paraffinlike substance, which was not investigated further. Hofmann [5], who obtained the same acid by oxidation of the phosphine, described it as a liquid, insoluble in water.

SUMMARY

1. Certain alkylphosphonous esters have been synthesized.

2. Their ability to combine with halogen, sulfur, and selenium and to undergo oxidation has been demonstrated.

3. The ability of ethylphosphonous dichloride to unite readily with sulfur in presence of a catalyst has been demonstrated.

4. The greater ease with which the esters $RP(OR)_2$, as compared with the esters $P(OR)_3$ and $ArP(OR)_2$, undergo addition and isomerization reactions has been demonstrated, and an explanation has been given for this phenomenon.

5. Esters of dialkylphosphinic and alkylphosphonoselonic acids have been synthesized for the first time.

6. Methods have been given for the synthesis of alkylphosphonothionic acids.

LITERATURE CITED

[1] A. E. Arbuzov, "Catalysis Phenomena in the Reactions of Certain Phosphorus Compounds", Kazan, 1914.

[2] R. B. Fox, J. Am. Chem. Soc. 72, 4147 (1950).

[3] M. Kharasch, E. Jensen, S. Weinhause, J. Org. Chem. 14, 429, (1951).

[4] F. Guichard, Ber. 32, 1572 (1899).

[5] A. Hofmann, Ber. 4, 605 (1871).

Received June 23, 1952

S. M. Kirov Kazan Chemico-Tehnical Institute

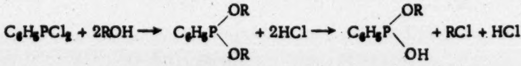
NEW METHOD FOR THE SYNTHESIS OF PHOSPHONIC AND PHOSPHINIC ESTERS AND THEIR THIO ANALOGS

COMMUNICATION 15. ADDITION OF PHENYL- AND ALKYL-PHOSPHONOUS ESTERS TO METHACRYLIC AND ACRYLIC ESTERS

A. N. Pudovik and D. Kh. Yarmukhametova

Esters of carboxy phosphonic (dihydroxyphosphinyl carboxylic) acids, as one of us has shown [1], may be readily prepared by the new method that we have developed for their synthesis: addition of dialkylphosphorous acids to α,β-unsaturated carboxylic esters. The reactions go very readily, in presence of a small amount of sodium alkoxide, and much heat is evolved; esters of carboxy phosphonic acids are obtained generally in high yield. Addition reactions have been carried out with equal success between dialkylphosphorous acids and esters of unsaturated dibasic acids: maleic, fumaric, and acetylenedicarboxylic. In the last case addition products were obtained which were formed by addition of two dialkylphosphorous acid molecules at the triple bond: esters of 1,2-dicarboxyethylenediphosphonic [α,β-bis(dihydroxyphosphinyl)succinic] acid.

We decided to study, as a development and extension of our previous work, the addition of partial esters of aryl- and alkyl-phosphonous acids to esters of unsaturated carboxylic acids. In this investigation we have chosen for study the addition of partial phenylphosphonous esters and of butyl hydrogen ethylphosphonite. It should be noted that aryl- and alkyl-phosphonous esters have received very little study. Only the butyl ester of phenylphosphonous acid is described [2] in the literature, and esters of alkylphosphonous acids were recently synthesized for the first time by B. A. Arbuzov and Rizpolozhensky [3], working in our laboratory. We have synthesized various esters of phenylphosphonous acid by the action of the corresponding alcohols on phenylphosphonous dichloride:

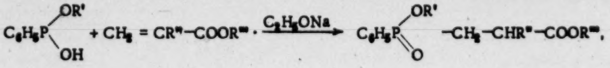


$$C_6H_5PCl_2 + 2ROH \rightarrow C_6H_5P\begin{matrix}OR\\ OR\end{matrix} + 2HCl \rightarrow C_6H_5P\begin{matrix}OR\\ OH\end{matrix} + RCl + HCl.$$

Constants and yields of the substances obtained are given in Table 1.

It should be noted that ethyl hydrogen phenylphosphonite, in spite of the contrary findings of Kosolapoff, was very readily prepared in good yield and had a characteristic odor, similar to that of other members of the series. We therefore found it quite possible to characterize it as a pure, individual substance and to apply it in synthesis. In our examination of the series of partial phenylphosphonous esters that we have prepared we gave some consideration to the rather considerable discrepancy between the calculated and determined values of the molecular refraction. In all cases the determined molecular refraction exceeded the calculated value by 1.1-1.5, which can evidently be explained by the constitutive effect of the phenyl group on the atomic refraction of phosphorus.

The addition of partial esters of phenylphosphonous acid to methacrylic and acrylic esters was effected by us by the usual procedure, which is described in detail in previous papers [4]. The reactions were very vigorous, and much heat was evolved. A solution of sodium ethoxide in absolute ethanol was used as catalyst: no exchange of radicals between alcohol and ester was observed, products of sharp boiling point being obtained in all cases, without any detectable by-products. The reactions went according to the equation:



$$C_6H_5P\begin{matrix}OR'\\ OH\end{matrix} + CH_2 = CR''-COOR''' \xrightarrow{C_2H_5ONa} C_6H_5P\begin{matrix}OR'\\ O\end{matrix}-CH_2-CHR''-COOR''',$$

where $R' = C_2H_5, C_4H_9, C_6H_{13}$, $R'' = H$ or CH_3; $R''' = CH_3, C_2H_5, C_3H_7$.

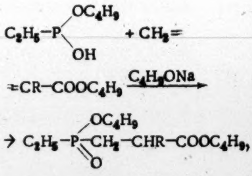
TABLE 1

No.	Formula	B.p. (°C/1 mm)	n_D^{20}	d_4^{20}	Yield (%)
1	$\begin{matrix}C_6H_5\\CH_3O\end{matrix}\!>\!POH$	91-93	1.5322	1.1770	66
2	$\begin{matrix}C_6H_5\\C_2H_5O\end{matrix}\!>\!POH$	94-95	1.5231	1.1291	84
3	$\begin{matrix}C_6H_5\\i\text{-}C_3H_7O\end{matrix}\!>\!POH$	106-107	1.5111	1.0922	70
4	$\begin{matrix}C_6H_5\\i\text{-}C_4H_9O\end{matrix}\!>\!POH$	112-113	1.5081	1.0675	88
5	$\begin{matrix}C_6H_5\\n\text{-}C_6H_{13}O\end{matrix}\!>\!POH$	139	1.5030	1.0388	60
6	$\begin{matrix}C_6H_5\\n\text{-}C_7H_{15}O\end{matrix}\!>\!POH$	150	1.4996	1.0187	80
7	$\begin{matrix}C_6H_5\\n\text{-}C_8H_{17}O\end{matrix}\!>\!POH$	155	1,4982	1.0079	78
8	$\begin{matrix}C_6H_5\\n\text{-}C_9H_{19}O\end{matrix}\!>\!POH$	158-160	1.4900	0.9843	57

TABLE 2

No.	Formula	B.p. (°C)	Pressure (mm Hg)	n_D^{20}	d_4^{20}	Yield (%)
1	$\begin{matrix}C_6H_5\\C_2H_5O\end{matrix}\!>\!\overset{O}{\overset{\Vert}{P}}\!-\!CH_2\!-\!\overset{CH_3}{\overset{\vert}{CH}}\!-\!COOCH_3$	141-143	0.5	1.5064	1.1390	72
2	$\begin{matrix}C_6H_5\\C_2H_5O\end{matrix}\!>\!\overset{O}{\overset{\Vert}{P}}\!-\!CH_2\!-\!CH_2\!-\!COOCH_3$	159-160	2	1.5081	1.1619	76
3	$\begin{matrix}C_6H_5\\C_2H_5O\end{matrix}\!>\!\overset{O}{\overset{\Vert}{P}}\!-\!CH_2\!-\!\overset{CH_3}{\overset{\vert}{CH}}\!-\!COOC_2H_5$	159-160	1	1.4992	1.1140	82
4	$\begin{matrix}C_6H_5\\C_2H_5O\end{matrix}\!>\!\overset{O}{\overset{\Vert}{P}}\!-\!CH_2\!-\!\overset{CH_3}{\overset{\vert}{CH}}\!-\!COOC_3H_7$	149	0.6	1.4962	1.0988	74
5	$\begin{matrix}C_6H_5\\i\text{-}C_4H_9O\end{matrix}\!>\!\overset{O}{\overset{\Vert}{P}}\!-\!CH_2\!-\!\overset{CH_3}{\overset{\vert}{CH}}\!-\!COOCH_3$	156	1	1.4965	1.0962	45
6	$\begin{matrix}C_6H_5\\C_6H_{13}O\end{matrix}\!>\!\overset{O}{\overset{\Vert}{P}}\!-\!CH_2\!-\!\overset{CH_3}{\overset{\vert}{CH}}\!-\!COOCH_3$	176-177	1	1.4908	1.0589	40
7	$\begin{matrix}C_2H_5\\C_4H_9O\end{matrix}\!>\!\overset{O}{\overset{\Vert}{P}}\!-\!CH_2\!-\!\overset{CH_3}{\overset{\vert}{CH}}\!-\!COOC_4H_9$	137-138	1	1.4490	1.0025	75
8	$\begin{matrix}C_2H_5\\C_4H_9O\end{matrix}\!>\!\overset{O}{\overset{\Vert}{P}}\!-\!CH_2CH_2COOC_4H_9$	141	1	1.4490	1.0146	74

When reactions were carried out under similar conditions between partial esters of alkylphosphonous acids and various esters of acrylic and methacrylic acids, we were unable to obtain completely pure products. Most of them had a wide boiling range (3-5°), and besides the main product appreciable amounts of lower- and higher-boiling fractions were obtained. Since the contamination of the main reaction product could arise from secondary products formed as a result of radical exchange between ester and alcohol groups, we carried out experiments in which the radicals of the ester groups and of the alcohol used for preparation of alkoxide were identical. We then obtained addition products having sharp boiling points: their phosphorus contents corresponded accurately to the calculated values. The reaction was as follows:



$$C_2H_5\!-\!P\begin{matrix}OC_4H_9\\OH\end{matrix} + CH_2{=}CR\!-\!COOC_4H_9 \xrightarrow{C_4H_9ONa} C_2H_5\!-\!\underset{O}{\underset{\Vert}{P}}\overset{OC_4H_9}{\,}\!-\!CH_2\!-\!CHR\!-\!COOC_4H_9,$$

where R = H or CH_3.

Constants and yields of addition products formed by partial phenyl- and ethylphosphonous esters with acrylic and methacrylic esters are given in Table 2.

EXPERIMENTAL

Prepration of Alkyl Hydrogen Phenylphosphonites.

Methyl hydrogen phenylphosphonite. Phenylphosphonous dichloride (14.6 g) was added dropwise to absolute methanol (15 g) contained in an Arbuzov flask. Hydrogen chloride was drawn off over a period of 3-4 hours, and the reaction mixture was then vacuum-fractionated, yielding methyl hydrogen phenylphosphonite (8.4 g).

Found %: P 19.89; 20.23
$C_7H_9O_2P$. Calculated %: P 19.87

Ethyl hydrogen phenylphosphonite. The procedure was similar to that of the previous experiment. Phenylphosphonous dichloride (25 g) and absolute ethanol (20 g) yielded ethyl hydrogen phenylphosphonite (20 g).

Found %: P 18.11; 17.92
$C_8H_{11}O_2P$. Calculated %: P 18.23

Isopropyl hydrogen phenylphosphonite. Phenylphosphonous dichloride (11.3 g) and absolute isopropyl alcohol (11.3 g) yielded isopropyl hydrogen phenylphosphonite (9.3 g).

Found %: P 16.86; 16.67
$C_9H_{13}O_2P$. Calculated %: P 16.85

Isobutyl hydrogen phenylphosphonite. Phenylphosphonous dichloride (14.8 g) and absolute isobutyl alcohol (18.5 g) yielded isobutyl hydrogen phenylphosphonite (14.4 g).

Found %: P 15.79
$C_{10}H_{15}O_2P$. Calculated %: P 15.66

Hexyl hydrogen phenylphosphonite. Phenylphosphonous dichloride (10.7 g) and dry hexyl alcohol (18.3 g) yielded hexyl hydrogen phenylphosphonite (8 g):

Found %: P 13.72
$C_{12}H_{19}O_2P$. Calculated %: P 13.48

Heptyl hydrogen phenylphosphonite. Phenylphosphonous dichloride (10 g) and heptyl alcohol (19 g) yielded heptyl hydrogen phenyl-phosphonite (10.7 g).

Found %: P 12.82; 12.18
$C_{13}H_{21}O_2P$. Calculated %: P 12.92

Octyl hydrogen phenylphosphonite. Phenylphosphonous dichloride (8.8 g) and octyl alcohol (19.2 g) yielded octyl hydrogen phenylphosphonite (9.6 g).

Found %: P 12.32
$C_{14}H_{23}O_2P$. Calculated %: P 12.20

Nonyl hydrogen phenylphosphonite. Phenylphosphonous dichloride (10 g) and nonyl alcohol (24 g) yielded nonyl hydrogen phenylphosphonite (8.5 g).

Found %: P 11.33
$C_{15}H_{25}O_2P$. Calculated %: P 11.57

Addition of Ethyl Hydrogen Phenylphosphonite to Methyl Methacrylate

The reaction was carried out in an Arbuzov flask. A saturated solution of sodium ethoxide (4-5 drops) was added to a mixture of ethyl hydrogen phenylphosphonite (7 g) and methyl methacrylate (4.1 g), and reaction proceeded with evolution of much heat. The reaction mixture was vacuum-distilled yielding ethyl (2-methoxycarbonylpropyl)phenyl phosphinate (8 g) having b.p. 141-143° at 0.5 mm; n_D^{20} 1.5064; d_4^{20} 1.1390.

Found %: P 11.78
$C_{13}H_{19}O_4P$. Calculated %: P 11.48

Addition of Ethyl Hydrogen Phenylphosphonite to Methyl Acrylate

The procedure was similar to that of the previous experiment. Ethyl hydrogen phenylphosphonite (5 g) and methyl acrylate (2.5 g) yielded ethyl (2-methoxycarbonylethyl)phenylphosphinate (5.7 g) having b.p. 159-160° at 2 mm; n_D^{20} 1.5081; d_4^{20} 1.1619.

Found %: P 12.46; 12.36
$C_{12}H_{17}O_4P$. Calculated %: P 12.11

Addition of Ethyl Hydrogen Phenylphosphonite to Ethyl Methacrylate

Ethyl hydrogen phenylphosphonite (3 g) and ethyl methacrylate (2 g) yielded ethyl (2-ethoxycarbonylpropyl) phenylphosphinate (4.1 g) having b.p. 159-160° at 1 mm; n_D^{20} 1.4992; d_4^{20} 1.1140

Found %: P 11.12; 11.07
$C_{14}H_{21}O_4P$. Calculated %: P 10.92

Addition of Ethyl Hydrogen Phenylphosphonite to Propyl Methacrylate

Ethyl hydrogen phenylphosphonite (3 g) and propyl methacrylate (2.3 g) yielded ethyl (2-propoxycarbonylpropyl)phenylphosphinate (4 g) having b.p. 149° at 1 mm; n_D^{20} 1.4962; d_4^{20} 1.0988.

Found %: P 10.35; 10.67
$C_{15}H_{23}O_4P$. Calculated %: P 10.40

Addition of Isobutyl Hydrogen Phenylphosphonite to Methyl Methacrylate

Isobutyl hydrogen phenylphosphonite (6.1 g) and methyl methacrylate (3 g) yielded isobutyl (2-methoxycarbonylpropyl)phenylphosphinate (4 g) having b.p. 156° or 1 mm; n_D^{20} 1.4965; d_4^{20} 1.0962

Found %: P 10.50; 10.47
$C_{15}H_{23}O_4P$. Calculated %: P 10.40

Addition of Hexyl Hydrogen Phenylphosphonite to Methyl Methacrylate

Hexyl hydrogen phenylphosphonite (4 g) and methyl methacrylate (1.8 g) yielded hexyl (2-methoxycarbonylpropyl)phenylphosphinate (2.3 g) having b.p. 176-177° at 1 mm; n_D^{20} 1.4908; d_4^{20} 1.0589.

Found %: P 9.25; 9.28
$C_{17}H_{27}O_4P$. Calculated %: P 9.20

Addition of Butyl Hydrogen Ethylphosphonite to Butyl Methacrylate

Butyl hydrogen ethylphosphonite (4 g) and butyl methacrylate (3.8 g) yielded butyl (2-butoxycarbonylpropyl) ethylphosphinate (5.9 g) having b.p. 137-138° at 1 mm; n_D^{20} 1.4490; d_4^{20} 1.0025.

Found %: P 10.89
$C_{14}H_{29}O_4P$. Calculated %: P 10.62

Addition of Butyl Hydrogen Ethylphosphonite to Butyl Acrylate

Butyl hydrogen ethylphosphonite (4 g) and butyl acrylate (3.4 g) yielded butyl (2-butoxycarbonylethyl)ethylphosphinate (5.5 g) having b.p. 141° at 1 mm; n_D^{20} 1.4490; d_4^{20} 1.0146.

Found %: P 11.12; 11.12
$C_{13}H_{27}O_4P$. Calculated %: P 11.15

SUMMARY

1. The methyl, ethyl, isopropyl, isobutyl, hexyl, heptyl, octyl, and nonyl partial esters of phenylphosphonous acid have been synthesized.

2. It has been shown that, in presence of alkali-metal alkoxides, partial esters of phenylphosphonous and alkylphosphonous acids readily add on to methacrylic and acrylic esters.

3. Various esters of (2-alkoxycarbonylethyl)phenyl-, (2-alkoxycarbonylethyl)ethyl-, (2-alkoxycarbonylpropyl)phenyl-, and (2-alkoxycarbonylpropyl)ethyl-phosphinic acids have been synthesized.

LITERATURE CITED

[1] A.N. Pudovik, J. Gen. Chem., 22, 467, (1952).* [2] G. Kosolapoff, J. Am. Chem. Soc. 72, 4292 (1950). [3] B.A. Arbuzov and N.I. Rizpolozhensky, Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci., No. 5, 956, (1952).** [4] A. N. Pudovik, Proc. Acad. Sci. U.S.S.R., 73, 499 (1950).

Received June 23, 1952

A.E. Arbuzov Chemical Institute of the
Kazan Affiliated Institute of the
U.S.S.R. Academy of Sciences

---

* See Consultants Bureau translation, p 537.

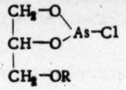
** See Consultants Bureau translation, p. 843.

PREPARATION OF CYCLIC ACID CHLORIDES AND MIXED ESTERS DERIVED FROM (ALKOXYMETHYL)ETHYLENE HYDROGEN ARSENITES AND TRIMETHYLENE HYDROGEN ARSENITE

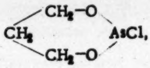
Gilm Kamai and N. A. Chadaeva

Acid chlorides derived from arsenious acid have received very little study in comparison with that received by acid chlorides derived from phosphorous acid. This situation probably arises from the difficulty with which the arsenic compounds are prepared and from their instability. Ethyl arsenodichloridite and diethyl arsenochloridite were prepared for the first time in 1920 by McKenzie and Wood [1] by the action of arsenic trichloride on sodium ethoxide. In 1951 Kamai and Khisamova [2] described the preparation and properties of the first cyclic acid chloride and of certain alkyl (and cycloalkyl) ethylene arsenites.

The object of the present investigation was the preparation of further cyclic acid chlorides and mixed esters, derived, in this case, from (alkoxymethyl)ethylene hydrogen arsenites and from trimethylene hydrogen arsenite. As a result of our experiments we have synthesized the following acid chlorides (arsenochloridites):

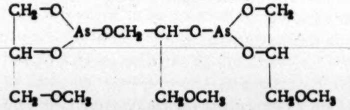


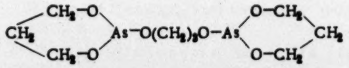
and



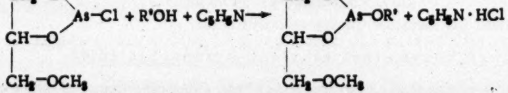
where R = CH_3, C_2H_5, i-C_3H_7, and n-C_4H_9.

In the synthesis of certain cyclic arsenochloridites in dry ether in presence of pyridine, we isolated the following full cyclic esters from the high-boiling fractions:





When these esters were heated with arsenic trichloride (equimolecular quantities), they were completely converted into the corresponding arsenochloridites. Also, by the reaction of (methoxymethyl)ethylene arsenochloridite with anhydrous alcohols in a medium of ether and pyridine, we have prepared various mixed esters:



By this method methyl, ethyl, propyl, butyl, hexyl, cyclohexyl, and phenyl (methoxymethyl)ethylene arsenites were prepared. These esters are colorless oils, readily miscible with many organic solvents and smelling, in some cases, rather like the original alcohols. They are hydrolyzed by water, giving arsenious oxide, 3-methoxy-1,2-propanediol, and the corresponding alcohols.

EXPERIMENTAL

Preparation of (Methoxymethyl)ethylene Arsenochloridite

Reaction carried out in absolute ether. A mixture of 3-methoxy-1,2-propanediol (32 g), freshly distilled pyridine (47.5 g) and about 400 ml absolute diethyl ether was introduced into a round-bottomed flask fitted with a mechanical stirrer, reflux condenser, and dropping funnel. The mixture was cooled to −5° and was stirred while 54.5 g arsenic trichloride was added from the dropping funnel. When about one-third of the total amount of arsenic trichloride had been added, a crystalline precipitate began to form. As soon as the calculated amount of arsenic trichloride had been added, cooling was discontinued, and the reaction mixture was heated on a water bath for one hour. It was allowed to stand overnight, and next day the ethereal solution was removed from the precipitate by decantation and the precipitate was washed three times with absolute ether. The solvent was driven off, and the residual liquid was vacuum-distilled, yielding the following two fractions:

Fraction I, b.p. 98-105°/10 mm;	43 g
Fraction II, b.p. 184-200°/3 mm;	8 g

In a second fractionation of Fraction I a cut of b.p. 102-104°/10 mm was taken.

Found %: As 35.25, 35.14; Cl 16.75

$C_4H_8O_3AsCl$. Calculated %: As 34.94; Cl 16.54

The product obtained was (methoxymethyl) ethylene arsenochloridite with the constants: d_0^0 1.7043; d_0^{20} 1.6771; n_D^{20} 1.5330; found MR_D 39.69; calculated for $C_4H_8O_3$ AsCl MR_D 39.45.

This arsenochloridite is a colorless liquid, soluble in ether, benzene, alcohol, carbon tetrachloride, and other organic solvents.

Fraction II also was fractionated further, yielding a product (1.7 g) of b.p. 197-200°/3 mm.

Found %: As 32.02, 32.52

$C_{12}H_{24}O_9As_2$. Calculated %: As 32.12

This substance is the full (methoxymethyl) ethylene ester of arsenious acid having the formula already cited; it has d_0^{20} 1.5762; d_0^{20} 1.5545; n_D^{20} 1.5095; found MR_D 86.26; calculated for $C_{12}H_{24}O_9As_2$ MR_D 86.63. It is a thick oil of good solubility in organic solvents.

Reaction in absence of solvent. Arsenic trichloride (55 g), contained in a flask, was heated to boiling, and 31 g 3-methoxy-1,2-propanediol was added from a dropping funnel. When the addition was complete, the reaction mixture was heated until evolution of hydrogen chloride ceased. The reaction mixture was then transferred to a distillation flask and was vacuum-distilled, yielding the following fractions:

Fraction I, b.p. 68-100°/11 mm;	18 g
Fraction II, b.p. 100-105°/11 mm;	45 g

Residue 3 g

Fraction II was analyzed without a second distillation:

Found %: As 34.16,34.17; Cl 17.13

$C_4H_8O_3AsCl$. Calculated %: As 34.94; Cl 16.54

According to the analytical data the substance was (methoxymethyl) ethylene arsenochloridite: d_0^0 1.7185; d_0^{20} 1.6880; n_D^{20} 1.5313; found MR_D 40.04; calculated for $C_4H_8O_3AsCl$ MR_D 39.45.

Hydrolysis of (Methoxymethyl) ethylene Arsenochloridite

A mixture of 3 g of (methoxy) ethylene arsenochloridite and 50 ml water was heated for one hour and then left overnight. The white precipitate that separated was filtered off, washed several times with water, dried to constant weight, and analyzed;

Found %: As 73.34, 73.35

As_2O_3. Calculated %: As 75.73

The white precipitate was therefore impure arsenious oxide.

Preparation of (Ethoxymethyl)ethylene Arsenochloridite

3-Ethoxy-1,2-propanediol (30 g) was added from a dropping funnel to 46.0 g boiling arsenic trichloride. After being heated for two hours, the reaction mixture was vacuum-fractionated:

Fraction I, b.p. 57-102°/13-10 mm;	5 g
Fraction II, b.p.102-113°/10 mm;	51 g

Residue 1.5 g

A second fractionation of Fraction II yielded 40 g of a product of b.p. 105.5-107°/9 mm.

Found %: As 32.99, 33.11; Cl 15.64,15.59

$C_5H_{10}O_3AsCl$. Calculated %: As 32.8; Cl 15.5

(Ethoxymethyl)ethylene arsenochloridite is a colorless liquid, soluble in many organic solvents; it has the constants: d_0^0 1.6132; d_0^{20} 1.5847; n_D^{20} 1.5160; found MR_D 43.55; calculated for $C_5H_{10}O_3AsCl$ MR_D 43.89.

Preparation of (Isopropoxymethyl)ethylene Arsenochloridite

Reaction of 41 g arsenic trichloride with 22 g 3-isopropoxy-1,2-propanediol yielded, by the method described for the previous arsenochloridites, 46 g of a substance of b.p. 110-117°/10 mm. A second distillation of this fraction yielded 35.6 g of a product of b.p. 114-116°/9 mm.

Found %: As 30.76, 30.84; Cl 14.15; 14.24

$C_6H_{12}O_3AsCl$. Calculated %: As 30.89; Cl 14.62

(Isopropoxymethyl)ethylene arsenochloridite is similar in properties to the arsenochloridites described above: d_0^0 1.5335; d_0^{20} 1.5060; n_D^{20} 1.5061; found MR_D 47.83; calculated for $C_6H_{12}O_3$ AsCl MR_D 48.59.

Preparation of (Butoxymethyl)ethylene Arsenochloridite

Reaction of arsenic trichloride (62 g) with 50 g 3-butoxy-1,2-propanediol (cf. preceding syntheses) yielded 60 g of a product with b.p. 129-130°/9 mm; d_0^0 1.4619; d_0^{20} 1.4273; n_D^{20} 1.5019; found MR_D 53.05; calculated for $C_7H_{14}O_3AsCl$ MR_D 53.11.

Found %: As 29.34, 29.22; Cl 13.89, 13.85

$C_7H_{14}O_3AsCl$. Calculated %: As 29.13; Cl 13.82

The arsenochloridite is a colorless, odorless liquid, soluble in organic solvents. It is readily hydrolyzed by water.

Preparation of (Chloromethyl)ethylene Arsenochloridite

Reaction of 37 g arsenic trichloride and 22 g 3-chloro-1,2-propanediol (cf. previous syntheses) yielded 18 g of a substance of b.p. 103-105°/11 mm.

Found %: As 33.95, 33.46; Cl 32.10

$C_3H_5O_2Cl_2As$. Calculated %: As 34.21; Cl 32.37

(Chloromethyl)ethylene arsenochloridite is a thick odorless liquid having d_0^0 1.9446; d_0^{20} 1.9131; n_D^{20} 1.5664; found MR_D 37.38; calculated for $C_3H_5O_2Cl_2As$ MR_D 38.2

Preparation of Trimethylene Arsenochloridite

Arsenic trichloride (80 g) was added to 30 g stirred cooled (−5°) mixture of 1,3-propanediol, 62.5 g freshly distilled pyridine, and 400 ml absolute diethyl ether. When the whole of the arsenic trichloride had been added, the reaction mixture was heated on a water bath for one hour and then allowed to stand overnight. Next day the ethereal solution was decanted from the crystalline precipitate, and the precipitate was washed three times with absolute ether. The solvent was driven off, and the residual liquid was vacuum-distilled. The following fractions were obtained:

Fraction I, b.p. 30-65°/10 mm;	10 g
Fraction II, b.p. 65-71°/10 mm;	34 g
Fraction III, b.p. 124-180°/2 mm;	16.5 g

A second fractionation of Fraction II yielded 21 g of a product of b.p. 66-67°/10 mm.

Found %: As 39.99, 40.29; Cl 19.04, 18.90

$C_3H_6O_2AsCl$. Calculated %: As 40.57; Cl 19.22

This product is trimethylene arsenochloridite and has the constants: d_0^0 1.7938; d_0^{20} 1.7624; n_D^{20} 1.5418; found MR_D 32.95; calculated for $C_3H_6O_2AsCl$ MR_D 33.19.

Fraction III was also refractionated and yielded 4.2 g of a product of b.p. 164-167°/3 mm.

Found %: As 40.10

$C_9H_{18}O_6As_2$. Calculated %: As 40.21

The full trimethylene ester of arsenious acid is a very thick, clear, odorless liquid. It has d_0^0 1.8213; d_0^{20} 1.7954; n_D^{20} 1.5139.

Preparation of (Methoxymethyl)ethylene Methyl Arsenite

Sodium (3.54 g) was added under stirring to 50 ml methanol contained in a round-bottomed flask. The solution of methoxide was cooled to 0°, and 32.2 g (methoxymethyl)ethylene arsenochloridite was added from a dropping funnel. The first drops of the arsenochloridite caused the solution to become turbid. When the calculated amount had been added, the reaction mixture was heated on a water bath for one hour, and was then allowed to stand overnight. The sodium chloride formed was filtered off through a fine sintered-glass filter, and was washed twice with dry methanol. The solvent was driven off, and the residual liquid was vacuum-fractionated, yielding the fractions:

Fraction I, b.p. 39-90°/13 mm
Fraction II, b.p. 90-93°/13 mm
Fraction III, b.p. 200-218°/3-4 mm

Redistillation of Fraction II yielded 6 g of a product of b.p. 91-92°/11 mm.

Found %: As 35.46, 35.08
$C_5H_{11}O_4As$. Calculated %: As 35.66

(Methoxymethyl)ethylene methyl arsenite is a mobile, colorless liquid having a specific odor. It is readily soluble in ether, alcohols, benzene, and other organic solvents. It is rapidly hydrolyzed by water. It has d_0^0 1.5311; d_0^{20} 1.5044; n_D^{20} 1.4798; found MR_D 39.77; calculated for $C_5H_{11}O_4As$: MR_D 40.28.

Preparation of Ethyl (Methoxymethyl)ethylene Arsenite

(Methoxymethyl)ethylene arsenochloridite (21.5 g) was added to a cooled (0°) mixture of 4.6 g of dry ethanol, 7.9 g distilled pyridine, and 200 ml absolute diethyl ether. Toward the end of the addition, cooling was discontinued. When the calculated amount of the arsenochloridite had been added, the reaction mixture was heated on a water bath for one hour. On the next day the precipitate of pyridine hydrochloride was separated by decantation of the solution, and was washed several times with small amounts of dry ether. The solvent was distilled off, and the residual liquid was vacuum-fractionated, yielding the three fractions:

Fraction I, b.p. 58-87°/11 mm;	3 g
Fraction II, b.p. 88-103°/11 mm;	8.5 g
Fraction III, b.p. 168-185°/3 mm;	8.9 g

Redistillation of Fraction II yielded 3.9 g of a substance of b.p. 97-98°/10 mm.

Found %: As 33.23, 33.66
$C_6H_{13}O_4As$. Calculated %: As 33.43

Ethyl (methoxymethyl)ethylene arsenite is a clear, mobile liquid, readily hydrolyzed in damp air with formation of arsenious oxide. It has d_0^0 1.4378; d_0^{20} 1.4172; n_D^{20} 1.4788; found MR_D 44.82; calculated for $C_6H_{13}O_4As$ MR_D 44.79.

Preparation of (Methoxymethyl)ethylene Propyl Arsenite

(Methoxymethyl)ethylene arsenochloridite (33.0 g) was added to a stirred, cooled (0°) mixture of 9 g propyl alcohol, 11.4 g freshly distilled pyridine, and 200 ml absolute diethyl ether. After removal of pyridine hydrochloride and of solvent, the residual liquid was vacuum-fractionated:

Fraction I, b.p. 100-104°/12 mm	
Fraction II, b.p. 104.5-106°/12 mm;	22.5 g
Fraction III, b.p. 116-167°/3 mm	

Three further fractionations of Fraction II resulted in the isolation of 10 g of a product having b.p. 101-103°/12 mm.

Found %: As 32.26, 32.56; Cl 1.83
$C_7H_{15}O_4As$. Calculated %: As 31.46

This preparation of (methoxymethyl)ethylene propyl arsenite was not completely pure: it was contaminated with the original arsenochloridite, whose boiling point is very close to that of the mixed ester. The product had the constants: d_0^{20} 1.3781; n_D^{20} 1.4762, found MR_D 48.47; calculated $C_7H_{15}O_4As$: MR_D 49.12.

Preparation of Butyl (Methoxymethyl)ethylene Arsenite

Starting with butyl alcohol (9 g), 10 g pyridine, 150 ml absolute diethyl ether, and 30 g (methoxymethyl)-ethylene arsenochloridite and proceeding as in the previous syntheses, we obtained 20 g of a product of b.p. 122-124° /12 mm.

Found %: As 29.8, 29.47
$C_8H_{17}O_4As$. Calculated %: As 29.71.

Butyl (methoxymethyl)ethylene arsenite, like its analogs already described, is a colorless, mobile liquid having the specific odor of butyl alcohol. It has d_0^0 1.3481; d_0^{20} 1.3248; n_D^{20} 1.4731; found MR_D 53.39; calculated for $C_8H_{17}O_4As$: MR_D 54.14.

Preparation of Hexyl (Methoxymethyl)ethylene Arsenite

Starting with hexyl alcohol (11 g), 7.9 g pyridine, 200 ml absolute diethyl ether and 22 g (methoxymethyl)-ethylene arsenochloridite and proceeding as in the previous syntheses, we obtained 17 g of a product of b.p. 147-148° /11 mm, which was analyzed without redistillation:

Found %: As 27.01, 26.99

$C_{10}H_{27}O_4As$. Calculated %: As 26.73

Hexyl (methoxymethyl)ethylene arsenite is a liquid having a characteristic odor, reminiscent of the odor of hexyl alcohol. It is hydrolyzed by water. It has d_0^{20} 1.2618; d_0^{20} 1.2411; n_D^{20} 1.4703; found MR_D 63.05; calculated for $C_{10}H_{21}O_4As$; MR_D 63.38.

Preparation of Cyclohexyl (Methoxymethyl)ethylene Arsenite

Starting with 7.7 g cyclohexanol, 5.9 g pyridine, 200 ml absolute diethyl ether, and 16.3 g (methoxymethyl)ethylene arsenochloridite and proceeding as in the previous syntheses, we obtained, after a second distillation, 8 g of b.p. 140-142°/10 mm.

Found %: As 27.29, 27.3

$C_{10}H_{19}O_4As$. Calculated %: As 26.99

Cyclohexyl (methoxymethyl)ethylene arsenite is a clear oily liquid having d_0^0 1.3599; d_0^{20} 1.3376; n_D^{20} 1.4950; found MR_D 60.61; calculated for $C_{10}H_{19}O_4As$; MR_D 61.17.

Preparation of (Methoxymethyl)ethylene Phenyl Arsenite

Starting with freshly distilled phenol (19 g), dissolved in 400 ml absolute diethyl ether, 15.8 g pyridine, and 43 g (methoxymethyl)ethylene arsenochloridite and proceeding as in the previous syntheses, we obtained 12.2 g of a product of b.p. 162-163°/13 mm.

Found %: As 27.73, 27.58

$C_{10}H_{13}O_4As$. Calculated %: As 27.52

(Methoxymethyl)ethylene phenyl arsenite is a colorless, oily liquid having the characteristic odor of phenol. It is of good solubility in organic solvents. It is rapidly hydrolyzed by water. It has d_0^0 1.4787; d_0^{20} 1.4552; n_D^{20} 1.5520; found MR_D 59.52; calculated for $C_{10}H_{13}O_4As$; MR_D 61.30.

Reaction of the Full (Methoxymethyl)ethylene Ester of Arsenious Acid with Arsenic Trichloride

The full (methoxymethyl)ethylene ester of arsenious acid (12.8 g) was introduced into a round-bottomed flask provided with reflux condenser and dropping funnel. Arsenic trichloride (5.1 g) was added from the dropping funnel, addition being accompanied by shaking; heat was evolved. When the calculated amount of arsenic trichloride had been added, the reaction mixture was heated on an oil bath at 180-185° for 30 minutes. The mixture was then cooled and vacuum-fractionated, yielding:

Fraction I, b.p. 102-104°/12 mm

Fraction II, b.p. 105°/12 mm; 10.5 g

Fraction II was analyzed without being redistilled:

Found %: As 34.37; 34.03; Cl 16.27

$C_4H_8O_3AsCl$. Calculated %: As 34.94; Cl 16.54

The substance isolated was almost pure (methoxymethyl)ethylene arsenochloridite.

SUMMARY

1. A study has been made of new cyclic acid chlorides derived from (alkoxymethyl)ethylene hydrogen arsenites and from trimethylene hydrogen arsenite.

2. It has been found that, in the preparation of (methoxymethyl)ethylene arsenochloridite and of trimethylene arsenochloridite in a medium of ether and pyridine, full cyclic esters are formed at the same time.

3. Mixed arsenious esters containing the bivalent radical (methoxymethyl)ethylene have been investigated.

4. It has been shown that the arsenochloridites and mixed esters that have been synthesized are hydrolyzed by water with formation of arsenious oxide and of the corresponding glycols and alcohols.

A.E.Arbuzov Chemical Institute of the Kazan Affiliated Institute
of the USSR Academy of Sciences

Received June 23, 1952

LITERATURE CITED

[1] McKenzie and Wood. J. Chem.Soc., 117, 406 (1920).

[2] Gilm Kamai and Z.L.Khisamova. Proc.Acad.Sci.USSR, 76, 535 (1951).

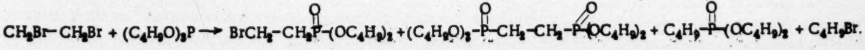
BLANK
PAGE

"PHOSPHONOETHYLATION" AND DIENE-SYNTHESIS REACTIONS WITH VINYLPHOSPHONIC ESTERS

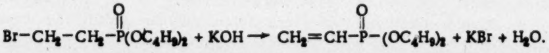
A.N.Pudovik and M.G.Imaev

α,β-Unsaturated phosphonic esters form a very interesting, but at the same time very little studied class of organophosphorus compounds. There are only brief mentions in the literature, occurring mainly in patents [1], concerning the preparation of individual α,β-unsaturated phosphonic acids other than diethyl vinylphosphonate. The methods proposed, however, involve starting materials that are not readily available, give low yields, and are often of poor reproducibility. The method that has received most attention is that used for the synthesis of the simplest representative of compounds of this type, diethyl vinylphosphonate, which was prepared by Kabachnik [2] and by Kosolapoff [3] from diethyl 2-chloro- or 2-bromo-ethylphosphonate by the splitting off of a molecule of hydrogen halide. The properties of vinylphosphonic esters have, prior to our work, remained practically without study. In a series of previous investigations one of us has shown [4] that the vinylphosphonic esters form a very reactive group of unsaturated compounds, which, in particular, are capable of undergoing various addition reactions, in which they exhibit strongly pronounced electrophilic character. In presence of alkali–metal alkoxides we have brought about addition to diethyl vinylphosphonate of the following compounds: dialkylphosphorous acids; ammonia and amines; and malonic, cyanoacetic, and acetoacetic esters and their homologs. In the majority of cases we obtained diethyl esters of β-substituted ethylphosphonic acids in high yield. To this reaction we gave the name "phosphonoethylation", since it brings about the introduction of the phosphonoethyl, i.e. dihydroxyphosphinylethyl, radical into nucleophilic organic compounds of a large variety of types.

In the present work, our previous investigations are continued: we have further shown the possibility of the addition to vinylphosphonic esters of hydrogen sulfide and mercaptans, and also the possibility of using vinylphosphonic acids as dienophiles in diene-synthesis reactions. In addition to diethyl vinylphosphonate, we have used the dibutyl ester, synthesized by a modification of the method of Kabachnik and Kosolapoff. In carrying out the reaction between ethylene dibromide and tributyl phosphite, we obtained, as by-products, dibutyl butylphosphonate and tetrabutyl ethylenediphosphonate:



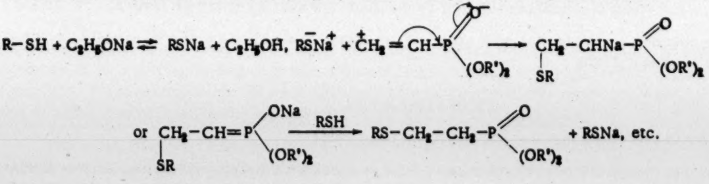
$$CH_2Br-CH_2Br + (C_4H_9O)_3P \rightarrow BrCH_2-CH_2\overset{O}{\overset{\|}{P}}-(OC_4H_9)_2 + (C_4H_9O)_2-\overset{O}{\overset{\|}{P}}-CH_2-CH_2-\overset{O}{\overset{\|}{P}}-(OC_4H_9)_2 + C_4H_9-\overset{O}{\overset{\|}{P}}-(OC_4H_9)_2 + C_4H_9Br.$$



$$Br-CH_2-CH_2-\overset{O}{\overset{\|}{P}}(OC_4H_9)_2 + KOH \rightarrow CH_2{=}CH-\overset{O}{\overset{\|}{P}}-(OC_4H_9)_2 + KBr + H_2O.$$

An attempt to prepare dimethyl vinylphosphonate was not successful: in the course of the reaction between ethylene dibromide and trimethyl phosphite, which was intended to yield dimethyl 2-bromoethylphosphonate, the trimethyl phosphite underwent rapid isomerization (owing to its high reactivity) under the influence of methyl bromide. The only reaction product was dimethyl methylphosphonate.

Addition of hydrogen sulfide and of ethanethiol to the diethyl and dibutyl esters of vinylphosphonic acid was carried out in absolute alcoholic solution in presence of sodium ethoxide. The reactions went readily even at room temperature; they proceeded more rapidly and with better yields at a higher temperature.



$$R-SH + C_2H_5ONa \rightleftharpoons RSNa + C_2H_5OH,\ R\bar{S}\overset{+}{Na} + \overset{+}{C}H_2{=}CH\overset{-}{-}P{\overset{\nearrow O}{\underset{\searrow (OR')_2}{}}} \longrightarrow \underset{SR}{\underset{|}{CH_2}}-CHNa-P{\overset{\nearrow O}{\underset{\searrow (OR')_2}{}}}$$

$$\text{or } \underset{SR}{\underset{|}{CH_2}}-CH{=}P{\overset{\nearrow ONa}{\underset{\searrow (OR')_2}{}}} \xrightarrow{RSH} RS-CH_2-CH_2-P{\overset{\nearrow O}{\underset{\searrow (OR')_2}{}}} + RSNa, \text{ etc.}$$

where R = H or C_2H_5, and R' = C_2H_5 or C_4H_9.

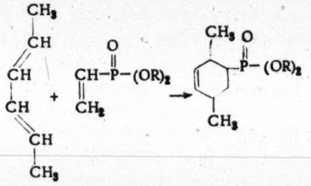
Constants and yields of the substances obtained are given in Table 1.

TABLE 1

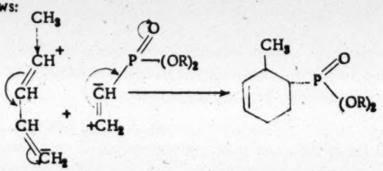
No.	Formula	B.p. (°C)	Pressure, mm Hg	n_D^{20}	d_4^{20}	Yield, %
1	$(C_2H_5O)_2\overset{O}{\overset{\Vert}{P}}-CH_2-CH_2-SH$	95-96	3	1,4210	1.0392	75.0
2	$(C_2H_5O)_2\overset{O}{\overset{\Vert}{P}}-CH_2-CH_2-SC_2H_5$	96	3	1.4265	1.0406	63.8
3	$(C_4H_9O)_2\overset{O}{\overset{\Vert}{P}}-CH_2CH_2SC_2H_5$	165-167	7	1.4580	1.0109	78.0

These addition products – diethyl 2-mercaptoethylphosphonate, diethyl 2-ethylmercaptoethylphosphonate, and dibutyl 2-ethylmercaptoethylphosphonate – are liquids having an unpleasant odor characteristic of aliphatic sulfides, but weaker; they are insoluble in water, but of good solubility in alcohol.

We then proceeded to the study of the diene-synthesis reaction, using vinylphosphonic esters as dienophilic components. This type of diene synthesis has not been studied before. It is of interest on this account and is also of great interest in the chemistry of organophosphorus compounds since it makes possible the synthesis of phosphonic esters containing a cyclohexenyl radical. In this work we used piperylene and hexadiene as dienes. The first exploratory experiments already showed that vinylphosphonic esters are considerably less reactive as dienophiles than, for example, α,β-unsaturated aldehydes, ketones, nitriles, and esters are. In order to obtain satisfactory yields in the reactions with piperylene and hexadiene, it was necessary to continue the reaction for 25-30 hours at temperatures of 170-180° and 270-280° respectively. With regard to the structures of the products obtained, no doubts arise in the case of the reaction with hexadiene, which, being symmetrical, may be expected to form only one adduct, the diethyl (dibutyl) ester of 2,5-dimethyl-3-cyclohexenylphosphonic acid:



but in the case of the reaction with piperylene two isomeric adducts are theoretically possible: esters of 2-methyl-3-cyclohexenylphosphonic and 5-methyl-3-cyclohexenylphosphonic acids. Recent investigations of B.A.Arbuzov and Kataev [5] and of A.A.Petrov and coworkers [6] have shown that the direction of addition of dienophiles to unsymmetrical dienes is in good agreement with the concepts of electronic theory. In our investigation, as in the investigations of these authors, the diene synthesis with piperylene yielded only one adduct, the formation of which may be represented as follows:



The constants and yields of substances obtained by the diene synthesis are given in Table 2.

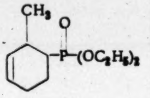
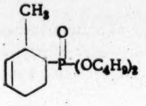
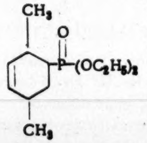
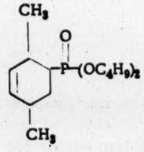
The adducts obtained are liquids having a weak but unpleasant odor.* They are of poor solubility in water, but dissolve readily in alcohol and ether.

EXPERIMENTAL

Action of Tributyl Phosphite on Ethylene Dibromide

The reaction was carried out in a round-bottomed flask provided with dropping funnel and Widmer fractionating column, which was joined to a condenser for the condensation of butyl bromide. Tributyl phosphite (30 g) was placed in the flask and was heated until the bath temperature reached 170°, when ethylene dibromide was slowly dropped in. During the reaction, the bath temperature was maintained at 170-190°. Altogether, 150 g of ethylene dibromide was added: a considerable amount of this was driven off during the reaction together with butyl bromide, for the boiling points of these two substances are very close together. Butyl bromide ceased to come over after 3 hrs. 30 min. Ethylene dibromide was driven off from the reaction mixture, and the residue was vacuum-distilled. After several fractionations we obtained about 2 g of dibutyl butylphosphonate and 19.8 g of dibutyl 2-bromoethylphosphonate, b.p. 146-147° at 5 mm; n_D^{20} 1.4485; d_4^{20} 1.1400. However, analysis for phosphorus and molecular-refraction calculations showed that the product obtained was not completely pure and contained, evidently, a small amount of dibutyl butylphosphonate (calculated %: P 10.3; found %: P 10.9), which boils at a temperature close to the boiling point of the main product.

TABLE 2

No.	Formula	B.p. °C	Pressure (mm Hg)	n_D^{20}	d_4^{20}	Yield %
1		118-119	3	1.4488	1.0166	63.5
2		155-156	3	1.4801	1.0379	65.2
3		125-127	7	1.4505	0.9992	44.0
4		156-157	2	1.4710	1.0042	36.4

From the residue we isolated 2.5 g of tetrabutyl 1,2-ethylenediphosphonate, b.p. 207-210°/7 mm; n_D^{20} 1.4402; d_4^{20} 1.0240; calculated MR_D 107.0; found MR_D 106.6.

Found %: P 15.3
$C_{18}H_{40}O_6P_2$. Calculated %: P 15.0.

An attempt was made to carry out the reaction by addition of the reactants in the reverse order, i.e., addition of tributyl phosphite to ethylene dibromide. However, the reaction did not go, for the temperature of the mixture did not attain the necessary value (170-190°).

Action of Alcoholic Potash on Dibutyl 2-Bromoethylphosphonate

An alcoholic solution of caustic potash (2.5 g) was added slowly (dropwise) to dibutyl 2-bromoethylphosphonate (15 g) dissolved in absolute ethanol (100 ml), the reaction mixture being stirred vigorously and cooled by surrounding the flask with ice. Addition of the alkali was accompanied by precipitation of potassium bromide. When reaction was complete, the precipitate was filtered off, and the alcohol was distilled from the filtrate. Vacuum distillation of the residue yielded dibutyl vinylphosphonate (7 g, 75%) having b.p. 115-116° at 5 mm; n_D^{20} 1.4372; d_4^{20} 0.9810; calculated MR_D 58.78; found MR_D 58.77.

Found %: P 14.4. $C_{10}H_{21}O_3P$. Calculated %: P 14.1

Action of Trimethyl Phosphite on Ethylene Dibromide

Trimethyl phosphite (40.5 g) and ethylene dibromide (100 g) were heated in a flask provided with a column for the removal of methyl bromide formed in the reaction. When the bath temperature reached 150°, profuse evolution of methyl bromide began; it was collected in a receiver cooled with a freezing mixture (10 g was collected). Fractionation of the reaction mixture yielded ethylene dibromide (50 g), trimethyl phosphite (15 g), and dimethyl methylphosphonate, b.p. 66-68°/8 mm; n_D^{20} 1.4135; d_4^{20} 1.1684.

The constants given in the literature [6] are: b.p. 181°/760 mm; n_D^{20} 1.4146; d_4^{20} 1.1684. There was a resinous residue, which decomposed when attempts were made to fractionate it under reduced pressure.

Addition of Hydrogen Sulfide to Diethyl Vinylphosphonate

Hydrogen sulfide was passed at room temperature through a solution of diethyl vinylphosphonate (6 g) in absolute ethanol (42 g) containing sodium ethoxide (0.3 g), until the mixture was completely saturated. After the mixture had stood for one day at room temperature, the alcohol was driven off, and the residue was vacuum-distilled, yielding 3 g of the originalvinylphosphonic ester and 2.5 g of diethyl 2-mercaptoethylphosphonate, which had b.p. 95-96°/3 mm; n_D^{20} 1.4210; d_4^{20} 1.0392; calculated MR_D 48.46; found MR_D 48.25.

Found %: P 15.30
$C_6H_{15}O_3SP$. Calculated %: P 15.62

In a second experiment the reaction was carried out in a sealed tube heated on a water bath for 15 hours. The yield was increased to 75%.

Addition of Ethanethiol to Diethyl Vinylphosphonate

A mixture of diethyl vinylphosphonate (5 g) and ethanethiol (4 g) was heated in presence of sodium ethoxide (0.3 g) in a sealed tube on a water bath for 18 hours. The tube was opened, the excess of ethanethiol was distilled off, and the residue was fractionated, yielding diethyl 2-ethylmercaptoethylphosphonate, b.p. 95-96°/4 mm; n_D^{20} 1.4265; d_4^{20} 1.0406; calculated MR_D 55.51; found MR_D 55.73.

Found %: P 13.72
$C_8H_{19}O_3PS$. Calculated %: P13.70

Addition of Ethanethiol to Dibutyl Vinylphosphonate

The reaction of dibutyl vinylphosphonate (5 g) with ethanethiol (4.5 g) in presence of sodium butoxide was carried out in a sealed tube heated in a water bath. Fractionation of the reaction mixture yielded dibutyl 2-ethylmercaptoethylphosphonate, b.p. 165-167°/7 mm; n_D^{20} 1.4580; d_4^{20} 1.0109; calculated MR_D 75.98; found MR_D 76.12.

Found %: P 11.4
$C_{12}H_{27}O_3PS$. Calculated %: P 11.0

Diene-synthesis Reactions of Piperylene and Hexadiene with Vinylphonic Esters

1. Reaction between piperylene and diethyl vinylphosphonate. A mixture of diethyl vinylphosphonate (7 g) and piperylene (10 g) was heated in presence of quinol (0.1 g) in a sealed tube at 170-180° for 25 hours. The excess of piperylene was distilled off, and the residue was vacuum-distilled, yielding some dimer of piperylene (about 3 g), unchanged vinylphosphonic ester (3.5 g), and diethyl 2-methyl-3-cyclohexenylphosphonate (3.5 g), which after two fractionations had b.p. 118-119°/3 mm; n_D^{20} 1.4488; d_4^{20} 1.0166; calculated MR_D 61.2; found MR_D 61.1. The residue was a resin.

Found %: P 13.40
$C_{11}H_{21}O_3P$. Calculated %: P 13.36

2. Reaction between piperylene and dibutyl vinylphosphonate. A mixture of dibutyl vinylphosphonate (3.7 g), piperylene (14 g), and quinol (0.1 g) was heated in a sealed tube at 190-200° for 25 hours. When the piperylene and its dimer had been driven off, the residue was distilled twice in a high vacuum and yielded dibutyl 2-methyl-3-cyclohexenylphosphonate, b.p. 155-156°/3 mm; n_D^{20} 1.4801; d_4^{20} 1.0379; calculated MR_D 79.7; found MR_D 78.8. The residue was a resin

Found %: P 11.0
$C_{15}H_{29}O_3P$. Calculated %: P 10.8

3. Reaction between hexadiene and diethyl vinylphosphonate. A mixture of diethyl vinylphosphonate (3 g), 2,4-hexadiene (10 g), and quinol (0.1 g) was heated in a sealed tube at 250-270° for 25 hours. Fractionation of the reaction mixture yielded diethyl 2,5-dimethyl-3-cyclohexenylphosphonate, b.p. 125-127°/7 mm; n_D^{20} 1.4505; d_4^{20} 0.9992; calculated MR_D 65.82; found MR_D 66.23.

Found %: P 12.7
$C_{12}H_{23}O_3P$. Calculated %: P12.6

4. Reaction between hexadiene and dibutyl vinylphosphonate. A mixture of dibutyl vinylphosphonate (4 g) and hexadiene (10 g) was heated at 270-290° for 25 hours. Fractionation of the reaction mixture yielded some unchanged hexadiene, some dimer of hexadiene, some unchanged vinylphosphonic ester (about 0.5 g),

and dibutyl 2,5-dimethyl-3-cyclohexenylphosphonate (2 g) having b.p. 154-156°/3 mm; n_D^{20} 1.4710; d_4^{20} 1.0042; calculated MR_D 84.29; found MR_D 84.06.

Found %: P 10.5
$C_{16}H_{31}O_3P$. Calculated %: P 10.3

SUMMARY

1. Dibutyl vinylphosphonate has been synthesized.

2. It has been shown that vinylphosphonic esters combine at the double bond with hydrogen sulfide and with mercaptans, yielding the corresponding dialkyl 2-mercaptoethylphosphonates and dialkyl 2-alkylmercaptoethylphosphonates respectively.

3. It has been shown that vinylphosphonic esters may be used as dienophiles in diene-synthesis reactions. A method has been developed for the preparation of esters of homologs and derivatives of cyclohexenylphosphonic acid.

Received June 23, 1952

V. I. Ulyanov-Lenin Kazan State University

LITERATURE CITED

[1] Hamilton, U. S. Patent 2365466 and 2382309; G. Kosolapoff, U. S. patent 2389576 (Chem. Abs. 40, 1536, 1946); Toy, U. S. patent 2425766; E. Bergman and A. Bondi, Ber. 64, 1455 (1931); 66. 286 (1933); A. Ford-Moore and Williams, J. Chem. Soc. 1947, 1465.

[2] M. I. Kabachnik, Bull. Acad. Sci. USSR, Div. Chem. Sci. 223 (1947).

[3] G. Kosolapoff, J. Am. Chem. Soc. 70, 1971 (1948).

[4] A. N. Pudovik, Proc. Acad. Sci. USSR, 80, 65 (1951).

[5] Б. A. Arbuzov and E. G. Kataev, J. Gen. Chem. 20, 68 (1950). See Consultants Bureau translation, p.73.

[6] A. A. Petrov and coworkers, J. Gen. Chem., 17, 538, 1295, 1543 (1947); 18, 424, 1781, 2228 (1948).

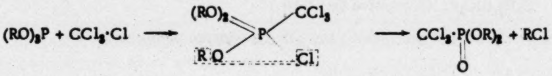
[illegible]

BLANK
PAGE

DECHLORINATION OF HEXACHLOROETHANE BY TRIALKYL PHOSPHITES

Gilm Kamai

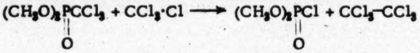
In a number of previous papers [1] it has been shown that carbon tetrachloride reacts fairly readily with many alkyl esters of phosphorous, alkylphosphonous, dialkylphosphinous, arylphosphonous, diarylphosphinous, pyrophosphorous, and hypophosphoric acids. Trialkyl phosphites react mainly according to the following scheme:



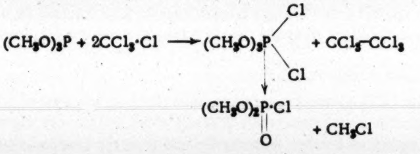
$$(RO)_3P + CCl_3\cdot Cl \longrightarrow \underset{\boxed{R}O\cdots\cdots\boxed{Cl}}{(RO)_2{=}P{-}CCl_3} \longrightarrow CCl_3\cdot\underset{\overset{\|}{O}}{P}(OR)_2 + RCl$$

However, the lowest member of these esters, trimethyl phosphite, forms an exception: it reacts with carbon tetrachloride in a more complicated fashion.

Reaction in accordance with the above scheme between trimethyl phosphite and carbon tetrachloride in equimolecular amounts will yield methyl chloride and methyl trichloromethylphosphonite, but it is probable that the latter ester then reacts with another molecule of carbon tetrachloride, forming hexachloroethane and dimethyl phosphorochloridate (Equation 1), or with two molecules of carbon tetrachloride, when intermolecular dechlorination occurs (Equation 2):

1. 

$$(CH_3O)_2\underset{\overset{\|}{O}}{P}CCl_3 + CCl_3\cdot Cl \longrightarrow (CH_3O)_2\underset{\overset{\|}{O}}{P}Cl + CCl_3{-}CCl_3$$

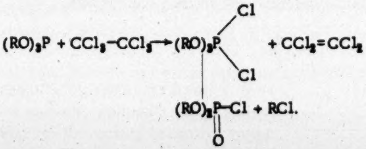
2. 

$$(CH_3O)_3P + 2CCl_3\cdot Cl \longrightarrow (CH_3O)_3PCl_2 + CCl_3{-}CCl_3$$
$$(CH_3O)_3PCl_2 \longrightarrow (CH_3O)_2\underset{\overset{\|}{O}}{P}\cdot Cl + CH_3Cl$$

It is interesting to note that trimethyl phosphite is here acting similarly to aluminum amalgam as a dechlorination agent in the formation of hexachloroethane from carbon tetrachloride.

It was considered that, if this second, intermolecular-dechlorination reaction did in fact occur, then it would undoubtedly be of interest to study the reaction between phosphorous esters and hexachloroethane itself.

With this object, experiments were carried out on the reactions of hexachloroethane with trimethyl, tripropyl, triisopropyl, and tributyl phosphites. As a result of these experiments it was established that, on being heated with an alkyl phosphite, hexachloroethane reacts very vigorously with formation of the corresponding alkyl chloride and dialkyl phosphorochloridate and of tetrachloroethylene. The reaction scheme is probably as follows:



$$(RO)_3P + CCl_3{-}CCl_3 \longrightarrow (RO)_3PCl_2 + CCl_2{=}CCl_2$$
$$(RO)_3PCl_2 \longrightarrow (RO)_2\underset{\overset{\|}{O}}{P}{-}Cl + RCl.$$

EXPERIMENTAL

Action of Hexachloroethane on Tributyl Phosphite

A mixture of tributyl phosphite (15 g) and hexachloroethane (14.2 g) was heated cautiously in the distilling flask of an Arbuzov assembly. At a bath temperature of about 100-105° the reaction became very vigorous with evolution of a substance of b.p. 78.5°, and external cooling was applied. By slow heating of the reaction mixture, Fraction I (5.3 g) of b.p. 78-80° and d_0^0 0.9069 was isolated; according to its properties, this fraction was relatively pure butyl chloride. The liquid remaining in the flask was vacuum-distilled; first at 28-30 mm (water pump), when Fraction II (6.8 g) came over at 38-40°; then at 4 mm (oil pump, when Fractions III (4.3 g) (b.p. 81-102°) and IV (7 g) (b.p. 102-104°)came over.

Redistillation of Fraction II yielded a liquid boiling at 121° under normal pressure; it had n_D^{20} 1.4998 and d_0^0 1.6298. According to its constants the substance was tetrachloroethylene.

Further fractionation of Fractions III and IV yielded a substance of b.p. 132-133°/15 mm; d_0^0 1.1442 and n_D^{20} 1.4341.

Found %: P 13.48
$C_8H_{18}ClO_3P$. Calculated %: P 13.76

According to the analytical data, this substance was dibutyl phosphorochloridate.

Action of Hexachloroethane on Tripropylphosphite

A mixture of tripropyl phosphite (15 g) and hexachloroethane (17 g) was heated slowly on an oil bath. Reaction set in at a bath temperature of about 100° with separation of propyl chloride. Fractionation yielded a propyl chloride fraction (4.9 g) of b.p. 46-47° and d_0^0 0.911 and a tetrachloroethylene fraction (9.1 g) of b.p. 121°; from the higher fractions a substance (6.8 g) of b.p. 107-108°/13 mm was isolated.

Found %: P 15.39
$C_6H_{14}ClO_3P$. Calculated %: P 15.47

Thus, according to the analytical data for phosphorus, the substance was dipropyl phosphorochloridate.

Action of Hexachloroethane on Triisopropyl phosphite

Careful heating of a mixture of triisopropyl phosphite (15 g) with hexachloroethane (16.9 g) yielded an isopropyl chloride fraction, b.p. 35-36° and d_0^{20} 0.8677, and a tetrachloroethylene fraction (8.9 g), b.p. 121°. Attempts to isolate diisopropyl phosphorochloridate from the higher fractions were not successful.

Action of Hexachloroethane on Trimethyl Phosphite

A mixture of trimethyl phosphite (12.4 g) and hexachloroethane (23.7 g) was heated cautiously in a flask fitted with reflux condenser. When the bath temperature reached about 90°, a very vigorous reaction set in, and it was therefore necessary to discontinue heating temporarily and to apply external cooling. The mixture was finally heated again for about two hours. The flask and contents were weighed before and after the heating, and the loss in weight was 6.9 g, instead of the theoretically required 5 g of methyl chloride. Fractional distillation yielded a tetrachloroethylene fraction (about 10 g). An attempt to separate dimethyl phosphorochloridate in the pure state was not successful.

I acknowledge my great indebtedness to L. A. Koroleva for the help she has given me in the experimental part of this work.

SUMMARY

1. It has been shown that, when trialkyl phosphites react with hexachloroethane, the corresponding alkyl chlorides and dialkyl phosphorochloridates are formed together with tetrachloroethylene.

2. It has been established that trialkyl phosphites may be used as dechlorinating agents for highly chlorinated paraffins.

Received June 23, 1952

S. M. Kirov Kazan Chemico-Technical Institute
A. E. Arbuzov Chemical Institute of the
Kazan Affiliated Institute of the USSR Academy
of Sciences

LITERATURE CITED

[1] Gilm Kamai, Proc.Acad. Sci. USSR, 55, 228 (1947); J. Gen. Chem. 16, 1522 (1946); Proc. Acad. Sci. USSR, 66, 388 (1949); 70, 233(1950); 79, 795 (1951).

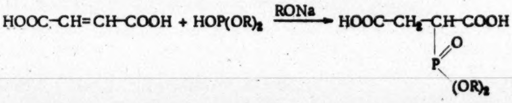
NEW METHOD FOR THE SYNTHESIS OF PHOSPHONIC AND PHOSPHINIC ESTERS AND THEIR THIO ANALOGS

COMMUNICATION 12. ADDITION OF DIALKYLPHOSPHOROUS ACIDS TO UNSATURATED DIBASIC ACIDS AND THEIR ESTERS

A. N. Pudovik

I have shown in previous papers [1] that dialkylphosphorous acids add very readily to esters of α,β-unsaturated monobasic acids in presence of alkali-metal alkoxides with formation of the corresponding β-dialkoxyphosphinyl carboxylic esters (esters of β-carboxyalkylphosphonic acids). Also, we have prepared, just as readily and in good yields, addition products formed by dialkylphosphorous acids with esters of ethylidenemalonic, benzylidene malonic, and acetoacetic esters.

We considered that it was of interest, as a development of our new method for the synthesis of phosphonic and phosphinic esters and, in particular, as a development of the investigations referred to above, to study the addition of dialkylphosphorous acids to certain symmetrical unsaturated dibasic acids and their esters. The unsaturated compounds that we chose for study were maleic and fumaric acids and their esters, and diethyl acetylenedicarboxylate. The reactions were carried out in presence of alkali-metal alkoxides in accordance with the usual procedure, which is described in detail in previous papers. Dialkylphosphorous acids in their reactions with maleic acid, to which they added very readily with considerable evolution of heat, showed behavior that contrasted sharply with that shown in previous, unsuccessful experiments on their addition to α,β-unsaturated monobasic acids. Dimethoxy- and diethoxy-phosphinylsuccinic acids were prepared in satisfactory yield.



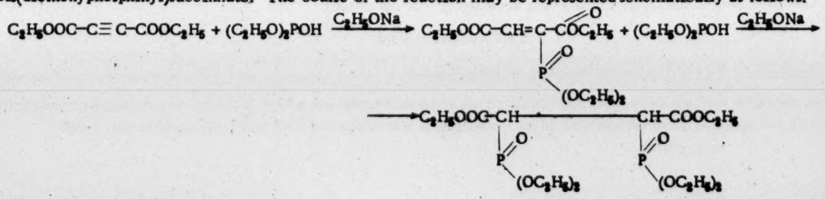
$$HOOC-CH=CH-COOH + HOP(OR)_2 \xrightarrow{RONa} HOOC-CH_2-\underset{\underset{(OR)_2}{P=O}}{CH}-COOH$$

Dialkylphosphorous acids add to maleic anhydride just as vigorously, but decomposition occurs during the vacuum distillation of the reaction mixture, low-boiling products being formed.

Addition of dialkylphosphorous acids to maleic esters in presence of alkali-metal alkoxides proceeds very vigorously and is accompanied by a change in color of the reaction mixture and the evolution of much heat. Addition of dialkylphosphorous acids to fumaric ester proceeds just as vigorously. Constants and yields of the addition products formed by dialkylphosphorous acids with maleic acid, dimethyl maleate, and diethyl fumarate are given in the table.

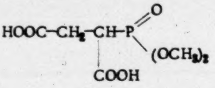
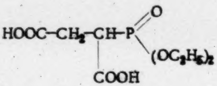
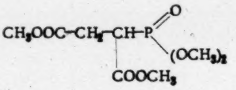
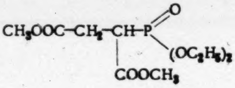
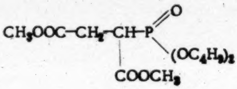
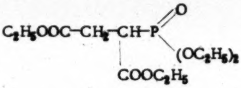
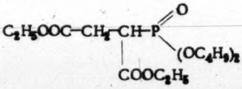
Attempts to bring about the addition of dialkylphosphorous acids to diethyl chlorofumarate, under our usual experimental conditions and also in presence of piperidine, were not successful.

Finally, a study was made of the addition of dialkylphosphorous acids to diethyl acetylenedicarboxylate. It might be expected that, depending on the ratio of reactants and experimental conditions, one or two molecules of dialkylphosphorous acid would add at the triple bond of acetylene dicarboxylic ester. Actually, when the molar ratio of diethylphosphorous acid to acetylenedicarboxylic ester was 2:1, only one addition product was obtained, and analysis for phosphorus, which was in accord with the empirical formula $C_{16}H_{32}O_{10}P_2$, indicated it to be diethyl bis(diethoxyphosphinyl)succinnate. The course of the reaction may be represented schematically as follows:



$$C_2H_5OOC-C\equiv C-COOC_2H_5 + (C_2H_5O)_2POH \xrightarrow{C_2H_5ONa} C_2H_5OOC-CH=\underset{\underset{(OC_2H_5)_2}{P=O}}{C}-\overset{O}{\overset{\|}{C}}OC_2H_5 + (C_2H_5O)_2POH \xrightarrow{C_2H_5ONa}$$

$$\longrightarrow C_2H_5OOC-\underset{\underset{(OC_2H_5)_2}{P=O}}{CH}-\underset{\underset{(OC_2H_5)_2}{P=O}}{CH}-COOC_2H_5$$

No.	Formula	B.p. °C	Pressure (mm Hg)	n_D^{20}	d_4^{20}	Yield %
1	 $HOOC-CH_2-CH(COOH)-P(=O)(OCH_3)_2$	141	3	1.4428	1.2695	50.0
2	 $HOOC-CH_2-CH(COOH)-P(=O)(OC_2H_5)_2$	137-138	1	1.4408	1.1782	70.8
3	 $CH_3OOC-CH_2-CH(COOCH_3)-P(=O)(OCH_3)_2$	142	2	1.4435	1.2076	78.0
4	 $CH_3OOC-CH_2-CH(COOCH_3)-P(=O)(OC_2H_5)_2$	184	13	1.4422	1.1803	81.9
5	 $CH_3OOC-CH_2-CH(COOCH_3)-P(=O)(OC_4H_9)_2$	161-162	1	1.4425	1.0666	69.7
6	 $C_2H_5OOC-CH_2-CH(COOC_2H_5)-P(=O)(OC_2H_5)_2$	161-162	2	1.4410	1.1333	82.3
7	 $C_2H_5OOC-CH_2-CH(COOC_2H_5)-P(=O)(OC_4H_9)_2$	178-179	2	1.4417	1.0673	95.7

A consideration of steric factors operating during the reaction indicates that the two diethoxyphosphinyl groups are probably attached to different carbon atoms, although their positions in the addition product were not determined precisely.

In a second experiment, carried out with the object of preparing the addition product formed from one molecule of diethylphosphorous acid and one of acetylenedicarboxylic ester, the reaction was performed in alcoholic solution and the amount of diethylphosphorous acid taken was half of that used before. However, also in this experiment, the only pure product obtained was bis(diethoxyphosphinyl)succinic ester; attempts to isolate a pure product from the low-boiling fraction (125-185°/8 mm) were not successful, in spite of repeated refractionations, for, although a fraction (b.p. 160-163°/3 mm) was obtained in small quantity and evidently consisted mainly of the required substance, it was contaminated (the discrepancy between the calculated and found phosphorus contents was about 1%).

Similarly, in the reaction between diethyl acetylenedicarboxylate and dimethylphosphorous acid, only diethyl bis(dimethoxyphosphinyl)succinate was obtained in the pure state.

EXPERIMENTAL

Addition of Dimethylphosphorous Acid to Maleic Acid

A saturated solution of sodium methoxide in absolute methanol was added dropwise to a mixture of maleic acid (4.2 g) and dimethylphosphorous acid (8 g). Addition of each drop resulted in a considerable rise in the temperature of the reaction mixture. Altogether, about ten drops were added, and further addition of methoxide did not produce a heating effect. Fractionation of the reaction mixture yielded dimethoxyphoshpinylsuccinic acid (4.1 g) having b.p. 141°/3 mm; n_D^{20} 1.4428; d_4^{20} 1.2695.

Found %: P 13.7; 13.9

$C_6H_{11}O_7P$. Calculated %: P 13.7

Addition of Diethylphosphorous Acid to Maleic Acid

Maleic acid (3 g) and diethylphosphorous acid (6 g) were taken for reaction, and ethanol was added to the mixture until the maleic acid was completely dissolved. The reaction was carried out in presence of sodium ethoxide. The reaction mixture was heated on a water bath for three hours; the alcohol was then distilled off, and the residue was vacuum-fractionated, yielding diethoxyphosphinylsuccinic acid (4.6 g) having b.p. 137-138° at 1 mm; n_D^{20} 1.4408; d_4^{20} 1.1782.

Found %: P 12.1; 12.0

$C_8H_{15}O_7P$. Calculated %: P 12.2

Addition of Dialkylphosphorous Acids to Maleic Anhydride

A mixture of maleic anhydride (8 g) and dimethylphosphorous acid (12 g) was heated in an Arbuzov flask on a water bath until the maleic anhydride had melted and dissolved. A solution of sodium methoxide in methanol was then added dropwise: evolution of heat occurred, but was not as great as in the maleic acid reaction. In the fractionation the temperature of the vapor rose to 105-110° at 7 mm pressure, and then vigorous decomposition set in. An attempt to add diethylphosphorous acid to maleic anhydride was also unsuccessful.

Addition of Dimethylphosphorous Acid to Dimethyl Maleate

Dimethyl maleate (7.2 g) and dimethylphosphorous acid (6 g) were taken for reaction. Addition of the first few drops of a solution of sodium methoxide in methanol brought about an extremely vigorous reaction accompanied by evolution of much heat and boiling of the reaction mixture (vaporization of methanol). The temperature of the reaction mixture rose to 70°. Further addition of methoxide was carried out while the mixture was cooled with water. Sufficient (about 20 drops in all) of the saturated sodium methoxide solution was added to complete the reaction, and the mixture was then heated for one hour on a water bath. It was then vacuum-fractionated: two fractionations yielded dimethyl dimethoxyphosphinylsuccinate (9.9 g) having b.p. 142°/2 mm; n_D^{20} 1.4435; d_4^{20} 1.2076.

Found %: P 11.9

$C_8H_{15}O_7P$. Calculated %: P 12.2

Addition of Diethylphosphorous Acid to Dimethyl Maleate

Dimethyl maleate (14.7 g) and diethylphosphorous acid (14 g) were taken for reaction, the catalyst being a solution of sodium ethoxide in ethanol. The procedure was similar to that of the preceding experiment, and fractionation of the reaction mixture yielded dimethyl diethoxyphosphinylsuccinate (23.6 g) having b.p. 184°/13 mm; n_D^{20} 1.4422; d_4^{20} 1.1803.

Found %: P 10.9; 10.8

$C_{10}H_{19}O_7P$. Calculated %: P 10.9

Addition of Dibutylphosphorous Acid to Dimethyl Maleate

Dibutylphosphorous acid (15 g) reacted with dimethyl maleate (10.7 g) in presence of sodium butoxide. Fractionation of the reaction mixture yielded dimethyl dibutoxyphosphinylsuccinate (17.9 g) having b.p. 161-162° at 1 mm; n_D^{20} 1.4425; d_4^{20} 1.0666.

Found %: P 8.8; 8.9

$C_{14}H_{27}O_7P$. Calculated %: P 9.2

Hydrolysis of Dimethyl Diethoxyphosphinylsuccinate

The ester (3.5 g) was hydrolyzed with dilute (1:1) hydrochloric acid in a sealed tube at 120-130° for six hours. Ethyl chloride was removed from the solution, which was then heated on a water bath, distilled water being added periodically to make up for losses by evaporation. When the whole of the hydrogen chloride present had been removed, the solution was carefully evaporated down, yielding dihydroxyphosphinylsuccinic acid as a thick yellowish oil, which did not crystallize after long standing in a desiccator (either at room temperature or under cooling).

Addition of Diethylphosphorous Acid to Diethyl Fumarate

Fumaric ester (6.8 g) and diethylphosphorous acid (6.5 g) were taken for reaction. Addition of ethoxide was accompanied by evolution of much heat. Fractionation yielded diethyl diethoxyphosphinylsuccinate (10.2 g) having b.p. 161-162°/2 mm, n_D^{20} 1.4410; d_4^{20} 1.1333.

Found %: P 10.3, 10.2

$C_{12}H_{23}O_7P$. Calculated %: P 10.0

Addition of Dibutylphosphorous Acid to Diethyl Fumarate

Fumaric ester (5.1 g) reacted with dibutylphosphorous acid (6 g) in presence of sodium butoxide, yielding diethyl dibutoxyphosphinylsuccinate (9.1 g) having b.p. 178-179° at 2 mm; n_D^{20} 1.4417; d_4^{20} 1.0673.

Found %: P 8.6

$C_{16}H_{31}O_7P$. Calculated %: P 8.5

Addition of Diethylphosphorous Acid to Diethyl Acetylenedicarboxylate

Expt. 1. Diethyl acetylenedicarboxylate (5.6 g) and diethylphosphorous acid (9.2 g) were taken for reaction. No heating effect occurred when the first few drops of ethoxide solution were added, but further addition caused the liquid to turn violet, and the mixture began to warm up rapidly, the temperature rising to 88°. The mixture was cooled and fractionated, yielding diethyl bis(diethoxyphosphinyl)succinate (6 g) having b.p. 213-214° at 5 mm; n_D^{20} 1.4700; d_4^{20} 1.3753.

Found %: P 14.1; 13.9

$C_{16}H_{32}O_{10}P_2$. Calculated %: P 13.9

Expt. 2. The reaction mixture, which consisted of acetylenedicarboxylic ester (7 g), diethylphosphorous acid (5.8 g), ethanol (20 ml), and ethoxide solution (1 ml), was heated on a water bath for three hours. Fractionation of the reaction mixture yielded diethyl bis(diethoxyphosphinyl)succinate (2.7 g), b.p. 210°, having constants identical with those obtained in the first experiment, and a fraction (5.6 g) of b.p. 125-185°/8 mm. In a second fractionation it again boiled over a wide temperature range, but the top cut, which had a stable boiling point of 160-163°/3 mm, contained 9.1% of phosphorus, compared with 10% required for the product formed by addition of one molecule of diethylphosphorous acid to acetylenedicarboxylic ester.

Addition of Dimethylphosphorous Acid to Diethyl Acetylenedicarboxylate

Acetylenedicarboxylic ester (14 g) reacted with dimethylphosphorous acid (9.5 g) in presence of sodium methoxide. The reaction was very vigorous: the temperature of the reaction mixture rose rapidly to 105°, and the color of the mixture gradually changed from pink to dark red. Fractionation of the reaction mixture yielded diethyl bis(dimethoxyphosphinyl)succinate (3.2 g) having b.p. 200-203°/3 mm; n_D^{20} 1.4635; d_4^{20} 1.2715, and also a fraction (15.6 g) of b.p. 70-200°/6 mm, which after repeated fractionation still boiled over a wide range of temperature.

Found %: P 15.5

$C_{12}H_{24}O_{10}P_2$. Calculated %: P 15.9

SUMMARY

1. It has been shown that, in presence of alkali-metal alkoxides, dialkylphosphorous acids readily add to maleic acid and to maleic and fumaric esters. The addition products have been obtained in good yield (dialkoxyphosphinylsuccinic acids and their esters).

2. It has been shown that under the same conditions, dialkylphosphorous acids add to diethyl acetylenedicarboxylate, and the products formed by addition of two molecules of dialkylphosphorous acid [bis(dialkoxyphosphinyl)succinic esters] have been isolated.

Received March 29, 1952

A. E. Arbuzov Chemical Institute of the Kazan
Affiliated Institute of the USSR Academy of Sciences

LITERATURE CITED

[1] A. N. Pudovik, J. Gen. Chem. 21, 1837 (1951); 22, 467 (1952). *

---

* See Consultants Bureau translation, p. 2035; p. 531.

NEW METHOD FOR THE SYNTHESIS OF PHOSPHONIC AND PHOSPHINIC ESTERS AND THEIR THIO ANALOGS

COMMUNICATION 13. ADDITION OF O,O-DIETHYL HYDROGEN PHOSPHOROTHIOITE TO KETONES AND ALDEHYDES

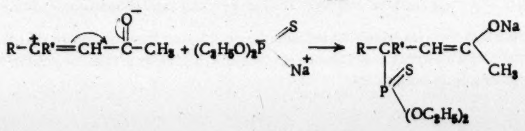
A. N. Pudovik and G. A. Zametaeva

In a number of previous papers [1] one of us has shown that dialkylphosphorous acids add very readily to unsaturated aldehydes and ketones in presence of alkali-metal alkoxides. Unsaturated aldehydes combine with dialkylphosphorous acids at the carbonyl group with formation of α-hydroxy phosphonic esters, but unsaturated ketones react at the double bond with formation of keto phosphonic esters. Only when selective addition of the first molecule is complete does further addition begin at the double bond or carbonyl group respectively of a second molecule of dialkylphosphorous acid (if excess of this is present in the reaction mixture) with formation of a hydroxy diphosphonic acid.

In connection with these investigations we considered that it was of interest to study the addition of O,O-dialkyl hydrogen phosphorothioites to unsaturated aldehydes and ketones and to compare the behavior of these esters in addition reactions with that of the corresponding dialkyl hydrogen phosphites (dialkylphosphorous acids). Also, this study could lead to the development of a method for the preparation of compounds of a new type — various derivatives of phosphonothionic esters.

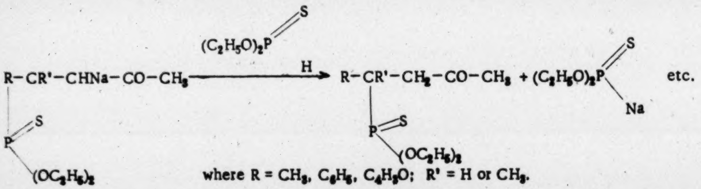
In the first series of experiments a study was made of the addition of O,O-diethyl hydrogen phosphorothioite to a number of unsaturated ketones; ethylideneacetone (3-penten-2-one), benzylideneacetone (4-phenyl-3-buten-2-one), furfurylideneacetone (4-furyl-3-buten-2-one), and mesityl oxide (4-methyl-3-penten-2-one). The reaction was carried out in presence of sodium ethoxide by the procedure described in previous papers. Addition proceeded very readily and was accompanied by a considerable evolution of heat. As in the addition of diethyl hydrogen phosphite to these compounds, it was found that reaction set in only after a definite amount of sodium ethoxide solution had been added and then went very rapidly, generally to completion. These peculiarities indicate that these reactions have certain definite characteristics: as we have pointed out previously, they proceed by a chain mechanism.

As in the reactions of dialkyl hydrogen phosphites, addition of O,O-diethyl hydrogen phosphorothioite proceeded most vigorously with ethylidene- and benzylidene-acetone, the addition products being obtained in 50-75% yield. An investigation of the properties of the addition products showed that they contained a free ketone group, for they formed phenylhydrazones and semicarbazones with phenylhydrazine and semicarbazide respectively; also, they were saturated: this was established by the aid of the bromination reaction. On the basis of these results the conclusion was reached that the products obtained were keto phosphonothionic esters and that addition of O,O-dialkyl hydrogen phosphorothioite to α,β-unsaturated ketones occurs in the first place at the double bond, which in these compounds is more active than the ketone group. The course of the addition reaction may be represented as follows:



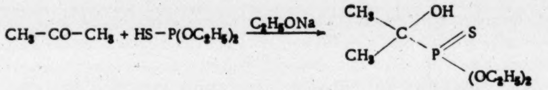
$$(C_2H_5O)_2PSH + C_2H_5ONa \rightleftharpoons (C_2H_5O)_2P\overset{S}{\underset{Na}{<}} + C_2H_5OH$$

or



where R = CH_3, C_6H_5, C_4H_3O; R' = H or CH_3.

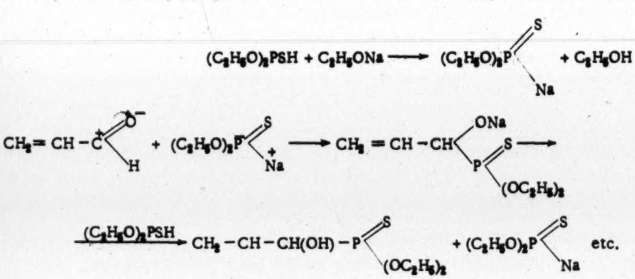
However, in the products obtained the ketone group also is able to combine with O,O-diethyl hydrogen phosphorothioite when there is an excess of the latter in the reaction mixture. We showed that this reaction is possible by special experiments on the simplest saturated ketone, acetone. Reaction went according to the equation



with formation of diethyl 1-hydroxy-1-methylethylphosphonothionate, i.e., in similar manner to the addition of dialkyl hydrogen phosphites to keto phosphonic esters, as noted in previous papers, and to the simplest saturated aldehydes and ketones, as described by Abramov [2]. Constants and yields of our addition products are given in Table 1.

A study was also made of the addition of O,O-diethyl hydrogen phosphorothioite to unsaturated and saturated aldehydes. Reactions with acrolein, crotonaldehyde, and 2-furanacrolein yielded addition products in about 50% yield, and it was found that they did not react with substances that readily react with the carbonyl group, including phenylhydrazine and semicarbazide.

Reaction with bromine indicated the presence of one double bond. The results obtained show definitely that the addition products formed by O,O-diethyl hydrogen phosphorothioite with unsaturated aldehydes are unsaturated α-hydroxy phosphonothionic esters and that addition therefore proceeds not at the double bond, as in unsaturated ketones, but at the carbonyl group. The course of the reaction may be represented as follows:



Similar experiments with acetaldehyde and butyraldehyde showed that addition of O,O-diethyl hydrogen phosphorothioite proceeds very readily also at the carbonyl group of a saturated aldehyde. Constants and yields of the addition products obtained — unsaturated and saturated α-hydroxy phosphonothionic esters — are given in Table 2.

From the investigations that we have carried out the conclusion may be drawn that in its addition reactions with unsaturated and saturated aldehydes and ketones O,O-diethyl hydrogen phosphorothioite exhibits the same specific reactivity as dialkyl hydrogen phosphites.

TABLE 1

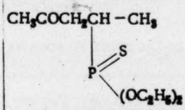
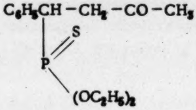
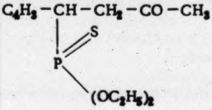
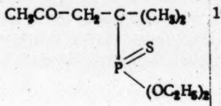
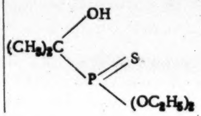
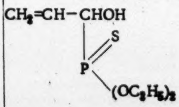
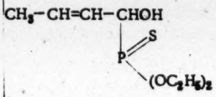
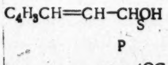
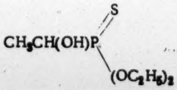
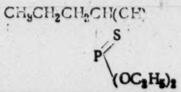
No	Formula	B.p. (°C)	Pressure (mm Hg)	n_D^{20}	d_4^{20}	Yield (%)
1	 $CH_3COCH_2CH(-CH_3)P(=S)(OC_2H_5)_2$	142-144	12	1.4638	1.0549	50.1
2	 $C_6H_5CH(-CH_2-CO-CH_3)P(=S)(OC_2H_5)_2$	177-178	7	1.5344	1.1462	46.5
3	 $C_4H_3-CH(-CH_2-CO-CH_3)P(=S)(OC_2H_5)_2$	164-166	7	1.5025	1.1471	48.7
4	 $CH_3CO-CH_2-C(CH_3)_2P(=S)(OC_2H_5)_2$	128-130	7	1.4731	1.0590	74.1
5	 $(CH_3)_2C(OH)P(=S)(OC_2H_5)_2$	107-109	10	1.4684	1.0735	62.1

TABLE 2

No	Formula	B.p. (°C)	Pressure (mm Hg)	n_D^{20}	d_4^{20}	Yield (%)
1	 $CH_2=CH-CHOH-P(=S)(OC_2H_5)_2$	120-122	10	1.4828	1.1158	46.2
2	 $CH_3-CH=CH-CHOH-P(=S)(OC_2H_5)_2$	130-132	8	1.4846	1.1019	43.7
3	 $C_4H_3CH=CH-CHOH-P(=S)(OC_2H_5)_2$	101-102	10	1.5280	1.0785	46.1
4	 $CH_3CH(OH)P(=S)(OC_2H_5)_2$	111-113	12	1.4721	1.1029	62.3
5	 $CH_3CH_2CH_2CH(CH$ … $P(=S)(OC_2H_5)_2$	122-123	7	1.4761	1.0525	45.4

EXPERIMENTAL•

Addition of O,O-Diethyl Hydrogen Phosphorothioite to Ethylideneacetone. O,O-Diethyl hydrogen phosphorothioite (8 g) was caused to react with 4.4 g ethylideneacetone in presence of a saturated solution of sodium ethoxide. The reaction was accompanied by evolution of much heat. Thirty minutes after the completion of the reaction, the mixture was vacuum-distilled, yielding diethyl 1-methyl-3-oxobutylphosphonothionate (6.2 g) having b.p. 142-144/12 mm; n_D^{20} 1.4638; d_4^{20} 1.0549; found MR_D 62.23; calculated MR_D 62.22.

Found %: P 13.10

$C_9H_{19}O_3PS$. Calculated %: P 13.02

The addition product is a viscous, greenish oil of unpleasant odor.

Preparation of the phenylhydrazone. A mixture of the addition product (5 g), 2.3 g phenylhydrazine, and 6 ml absolute ethanol was placed in a porcelain dish and left in a desiccator for five days at room temperature. Vacuum distillation yielded 1.5 g of the phenylhydrazone of diethyl 1-methyl-3-oxobutylphosphonothionate (b.p. 238-240°/9 mm) as a thick, greasy, cherry-colored liquid. Some decomposition occurred during fractionation, and a dark-red resin remained as residue.

Found %: P 9.18, 8.99

$C_{15}H_{25}N_2O_2PS$. Calculated %: P 9.17

Preparation of the semicarbazone. Ethanol (5 ml) was added to a mixture of the addition product (1.5 g), semicarbazide hydrochloride (0.8 g) as an aqueous solution, and sodium acetate (0.6 g). The mixture was heated to boiling on a water bath, and was then

---

• O,O-Diethyl hydrogen phosphorothioite was prepared by the method developed in our laboratory; it had the following constants: b.p. 63° at 6 mm; n_D^{20} 1.4587; d_4^{20} 1.0763.

gradually cooled. After 2-3 hours white crystals (m.p. 124°) began to appear. Recrystallization from alcohol did not affect the melting point of the crystals obtained.

Found %: P 10.30
$C_{10}H_{22}N_3O_3PS$. Calculated %: P 10.51

Double-bond determination. A determination carried out by the McIlhiney method indicated an absence of double bonds.

Addition of O,O-Diethyl Hydrogen Phosphorothioite to Benzylideneacetone. The reaction was carried out with 5.3 g of O,O-diethyl hydrogen phosphorothioite and 5 g of benzylideneacetone in presence of sodium ethoxide, of which 15-20 drops were added in all; much heat was evolved. Fractionation of the reaction mixture yielded diethyl 1-phenyl-3-oxobutylphosphonothionate (4.6 g) having b.p. 177-178°/7 mm; n_D^{20} 1.5344; d_4^{20} 1.1462; found MR_D 81.41; calculated MR_D 81.7.

Found %: P 10.43
$C_{14}H_{21}O_3PS$. Calculated %: P 10.33

The addition product is a yellowish oil of unpleasant odor and of good solubility in alcohol and ether. A double-bond determination by the McIlhiney method showed that the substance is saturated.

Addition of O,O-Diethyl Hydrogen Phosphorothioite to Furfurylideneacetone. O,O-diethyl hydrogen phosphorothioite (6 g) reacted with furyfurylideneacetone (5 g) in presence of 10-15 drops of a saturated solution of sodium ethylate. Heat was evolved, but the mixture did not become heated to the same extent as in the ethylideneacetone and benzylideneacetone reactions. Fractionation yielded diethyl 1-furyl-3-oxobutylphosphonothionate (5.1 g) having b.p. 164-166°/7 mm; n_D^{20} 1.5025; d_4^{20} 1.1471; found MR_D 74.67; calculated MR_D 74.58.

Found %: P 10.78
$C_{12}H_{19}O_4PS$. Calculated %: P 10.69

The addition product is a pale-yellow, viscous liquid of unpleasant odor and of good solubility in alcohol and ether.

Addition of O,O-Diethyl Hydrogen Phosphorothioite to Mesityl Oxide. Sodium ethoxide (20 drops) was added to a mixture of O,O-diethyl hydrogen phosphorothioite (6.85 g) and mesityl oxide (5 g). Reaction set in, and the mixture became very hot. The mixture was heated on a water bath for 30 minutes and was then vacuum-fractionated, yielding diethyl 1,1-dimethyl-3-oxobutylphosphonothionate (8 g) having b.p. 128-130°/7 mm; n_D^{20} 1.4731; d_4^{20} 1.0590; found MR_D 66.76; calculated MR_D 66.84.

Found %: P 12.43
$C_{10}H_{21}O_3PS$. Calculated %: P 12.30

The addition product is a colorless mobile liquid of good solubility in alcohol and ether.

Preparation of the phenylhydrazone. A mixture of diethyl 1,1-dimethyl-3-oxobutylphosphonothionate (5.6 g), phenylhydrazine (2.4 g) and absolute ethanol (8 ml) was allowed to stand for ten days at room temperature and was then vacuum-fractionated, yielding the phenylhydrazone (5 g, 65.7%; b.p. 234-235°/12 mm), a light-brown, thick greasy liquid.

Found %: P 8.83; 8.84
$C_{16}H_{27}O_2N_2PS$. Calculated %: P 9.06

Preparation of the semicarbazone. The small amount of alcohol necessary to produce a clear solution was added to a mixture of diethyl 1,1-dimethyl-3-oxobutylphosphonothionate (2 g), semicarbazide hydrochloride (1.3 g) as an aqueous solution, and sodium acetate (1 g). The mixture was heated to boiling on a water bath and was then gradually cooled, first to room temperature, and then to 0°. After one hour, crystallization set in. The melting point of the crystals obtained was 121°, raised to 123° by recrystallization from alcohol.

Found %: P 10.39
$C_{11}H_{21}N_3O_3PS$. Calculated %: P 10.03

Addition of O,O-Diethyl Hydrogen Phosphorothioite to Acetone. Sodium ethoxide (25-30 drops) was added to a mixture of freshly distilled acetone (17 g) and O,O-diethyl hydrogen phosphorothioite (4.8 g).

Reaction did not begin until 15-18 drops of sodium ethoxide had been added, and when further additions were made it proceeded with slight warming of the mixture. The reaction mixture was heated on a water bath for two hours and was then vacuum-fractionated, yielding diethyl 1-hydroxy-1-methylethylphosphonothionate (4 g) having b.p. 107-109°/10 mm; n_D^{20} 1.4684; d_4^{20} 1.0735; found MR_D 54.93; calculated MR_D 54.50.

Found %: P 14.72
$C_7H_{17}O_3PS$. Calculated %: P 14.62

The addition product is a colorless liquid of unpleasant odor and of good solubility in alcohol and ether.

Found %: OH 7.9 (Tserevitinov's method)
Calculated %: OH 8.01

Addition of O,O-Diethyl Hydrogen Phosphorothioite to Acrolein. Sodium ethoxide (20 drops) was added slowly to a mixture of O,O-diethyl hydrogen phosphorothioite (10 g) and acrolein (quinol-stabilized, 3.6 g), contained in a water-cooled flask. Reaction set in, and the reaction mixture became very hot. The sodium ethoxide was neutralized with glacial acetic acid, and the mixture was then vacuum fractionated, yielding diethyl 1-hydroxy-2-propenylphosphonothionate (6 g) having b.p. 120-122°/10 mm; n_D^{20} 1.4828; d_4^{20} 1.1158; found MR_D 53.73; calculated MR_D 54.03.

Found %: P. 15.03
$C_7H_{15}O_3PS$. Calculated %: P 14.76

The addition product is a greenish viscous liquid of unpleasant odor and of good solubility in alcohol and ether.

Action of phenylhydrazine. A mixture of the addition product (2.3 g), phenylhydrazine (1.2 g), and absolute ethanol (6 ml) was allowed to stand for six days at room temperature and was then vacuum-fractionated. Unchanged phenylhydrazine (1.1 g) was isolated.

Action of semicarbazide. A mixture of the addition product (0.5 g), semicarbazide hydrochloride (0.4 g), and sodium acetate (0.3 g) was heated to boiling on a water bath and was then gradually cooled. No semicarbazone was obtained.

Double-bond determination. Substance taken: 0.2654 g; thiosulfate required for titration of the bromine that underwent addition: 20 ml (T = 0.02318). The addition reaction should have required 0.2022 g of bromine; 0.2377 g was, in fact, required.

Addition of O,O-Diethyl Hydrogen Phosphorothioite to Crotonaldehyde. Saturated sodium ethoxide solution was added to a mixture of O,O-diethyl hydrogen phosphorothioite (4.4 g) and crotonaldehyde (2 g); the reaction mixture grew very hot. Fractionation of the reaction mixture yielded diethyl-1-hydroxy-2-butenylphosphonothionate (2.4 g) having b.p. 130-132°/8 mm; n_D^{20} 1.4846; d_4^{20} 1.1019; found MR_D 58.22; calculated MR_D 58.64.

Found %: P 13.46; 13.55
$C_8H_{17}O_3PS$. Calculated %: P 13.83

The addition product is a yellow, mobile liquid, soluble in alcohol and ether.

Double-bond determination. According to calculation, the addition reaction required 0.2408 g of bromide, and actually 0.2128 g of bromine was consumed.

Addition of O,O-Diethyl Hydrogen Phosphorothioite to 2-Furanacrolein. Sodium ethoxide was added to a mixture of O,O-diethyl hydrogen phosphorothioite (4 g) and 2-furanacrolein (3.2 g) dissolved in absolute alcohol (6 ml). The heating up of the reaction mixture was not so marked as in the case of acrolein. Fractionation of the reaction mixture yielded diethyl 3-furyl-1-hydroxy-2-propenylphosphonothionate (2.8 g) having b.p. 101-102°/10 mm; n_D^{24} 1.5280; d_D^{40} 1.0785.

Found %: P 11.51
$C_{11}H_{17}O_4PS$. Calculated %: P 11.23

The addition product is a thick, yellow liquid, which crystallizes on standing. The crystals melt at 25-26°.

Addition of O,O-Diethyl Hydrogen Phosphorothioite to Acetaldehyde. A saturated solution of sodium ethoxide (20 drops) was added to a mixture of O,O-diethyl hydrogen phosphorothioite (5 g) and freshly distilled acetaldehyde (1.5 g). The reaction mixture became very hot, but the effect was not so marked as in the case of the unsaturated aldehydes. The reaction mixture was set aside for one day and then vacuum-fractionated, yielding diethyl 1-hydroxyethylphosphonothionate (4 g) having b.p. 111-113°/12 mm; n_D^{20} 1.4721; d_4^{20} 1.1029; found MR_D 50.28; calculated MR_D 49.88.

Found %: P 15.91
$C_6H_{15}O_3PS$. Calculated %: P 15.65

The addition product is a pale-yellow oil of unpleasant odor.

Addition of O,O-Diethyl Hydrogen Phosphorothioite to Butyraldehyde. O,O-Diethyl hydrogen phosphorothioite (6 g) and butyraldehyde (3 g) reacted in presence of sodium ethoxide; the reaction mixture became hot and more viscous. Fractionation yielded diethyl 1-hydroxybutylphosphonothionate (3.6 g) having b.p. 122-123°/7 mm; n_D^{20} 1.4781; d_4^{20} 1.0925; found MR_D 58.56; calculated MR_D 59.12.

Found %: P 13.59; 13.52
$C_8H_{19}O_3PS$. Calculated %: P 13.71

SUMMARY

1. It has been shown that O,O-diethyl hydrogen phosphorothioite in presence of sodium ethoxide reacts readily at the double bond of unsaturated ketones with formation of keto phosphonothionic esters. It adds to saturated ketones at the carbonyl group with formation of α-hydroxy phosphonothionic esters.

2. O,O-Diethyl hydrogen phosphorothioite adds at the carbonyl group of unsaturated and saturated aldehydes with formation, respectively, of unsaturated and saturated α-hydroxy phosphonothionic esters.

3. A method has been developed for the synthesis of keto phosphonothionic esters and of unsaturated and saturated α-hydroxy phosphonothionic esters.

Received June 23, 1952

V. I. Ulyanov-Lenin Kazan State University

LITERATURE CITED

[1] A. N. Pudovik, Proc. Acad. Sci. USSR, 73,3,499 (1950); A. N. Pudovik and Yu. P. Kitaev, J. Gen. Chem. 22, 467 (1952)*; A. N. Pudovik and B. A. Arbuzov Proc. Acad. Sci. USSR 73, 327 (1950).

[2] V. S. Abramov, Proc. Acad. Sci. USSR, 73, 487 (1950).

---

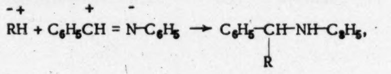
* See Consultants Bureau translation, p. 531.

NEW METHOD FOR THE SYNTHESIS OF PHOSPHONIC AND PHOSPHINIC ESTERS AND THEIR THIO ANALOGS

COMMUNICATION 14. NEW METHOD FOR THE SYNTHESIS OF AMINO PHOSPHONIC ESTERS

A. N. Pudovik and M. V. Korchemkina

In this paper a new method is proposed for the synthesis of amino phosphonic esters; it consists in the addition of dialkylphosphorous acids to anils. Anils are very reactive compounds and will combine at the double bond with various substances. Thus the simplest anil, N-benzylideneaniline, combines with bromine (giving a dibromide), and also with sodium bisulfite, ketones, amines, acetoacetic and malonic esters, hydrogen cyanide, nitromethane, organomagnesium compounds, and a number of other substances [1]. The direction of addition is determined by the polarization of the benzylideneaniline molecule and may be represented by the following general equation:



$$\overset{-+}{RH} + C_6H_5\overset{+}{C}H = \overset{-}{N}-C_6H_5 \rightarrow C_6H_5-\underset{\displaystyle R}{\underset{|}{C}H}-NH-C_6H_5,$$

where $R = -SO_3Na,\ -CH_2COR',\ -CN,\ CH_3CO\overset{|}{C}HCOOC_2H_5,\ -CH_2NO_2$

and R' is alkyl or aryl. In all cases the corresponding secondary aromatic amine derivatives are obtained.

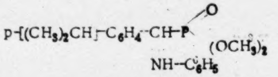
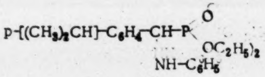
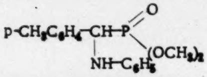
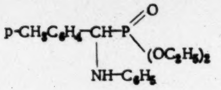
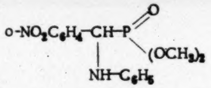
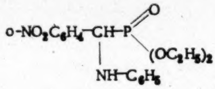
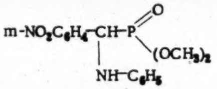
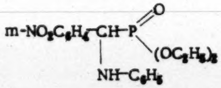
In connection with the investigations [2] carried out by one of us in the last few years on the addition of dialkylphosphorous acids to various unsaturated electrophilic reagents, for example, unsaturated ketones, aldehydes, nitriles, esters, acids, and vinylphosphonic esters, we considered that it was of great interest and importance to study the addition of dialkylphosphorous acids not only at double carbon — carbon and carbon — oxygen bonds, but also at double carbon — nitrogen bonds that are present in compounds of various types. We have embarked on this study, and have considered first the group of substituted aromatic imines obtained by the condensation of aromatic aldehydes and ketones with aniline derivatives. Preliminary work by Pudovik [3] has shown that, when the procedure that he has developed (reaction in presence of alkali-metal alkoxides [4]) is used, addition of dialkylphosphorous acids to the simplest anils (benzylideneaniline and certain of its derivatives) proceeds very readily, giving amino phosphonic esters in high yield. In our first series of experiments we have studied the addition of dimethyl- and diethyl-phosphorous acids to benzylideneaniline derivatives containing various substituents in the benzene nucleus of the benzylidene radical: (p-isopropyl-, (p-methyl-, (o-nitro-, (m-nitro-, and (o-hydroxy-benzylidene)aniline. The reaction was carried out in absolute ethanol in presence of sodium methoxide or ethoxide; the reaction mixtures became only slightly warm. The addition products were isolated by crystallization. Their melting points and yields, and the phosphorus-analysis results, are given in Table 1.

The addition products formed by dimethyl- and diethyl-phosphorous acids with (p-isopropylbenzylidene) aniline and (p-methylbenzylidene)aniline are white crystals of good solubility in ether and hot alcohol; they are insoluble in water. The addition products formed with (o- and (m-nitrobenzylidene)anilines are yellow substances. In the reactions of (o-hydroxybenzylidene)aniline (both with dimethyl- and with diethyl-phosphorous acid) a thick syrup was obtained which did not crystallize after long standing, and which decomposed when attempts were made to distil it under reduced pressure.

Further addition reactions of diethylphosphorous acid were carried out, namely, with N-benzylidine-p-chloroaniline and a number of anils having substituents in both benzene nuclei: N-(o-nitrobenzylidene)-m-toluidine, p-chloro-N-(p-isopropylbenzylidene)aniline, N-(p-methylbenzylidene)-m-toluidine, and N-(p-isopropylbenzylidene)-o-toluidine. The results obtained are given in Table 2.

All the reactions proceeded with slight evolution of heat. We synthesized the following anils derived from ketones in order to apply them in the addition reaction with diethylphosphorous acid: the anils derived from aniline

TABLE 1

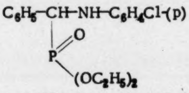
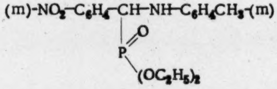
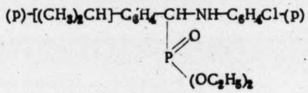
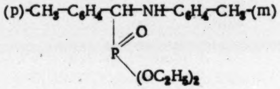
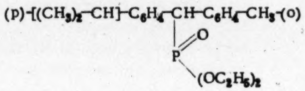
No.	Formula	M.p. (°C)	Yield (%)	Phosphorus (%)	
				found	calculated
1	 $p\text{-}[(CH_3)_2CH]\text{-}C_6H_4\text{-}\underset{NH-C_6H_5}{CH}\text{-}\overset{O}{P}(OCH_3)_2$	106-107	67.7	9.67	9.67
2	 $p\text{-}[(CH_3)_2CH]\text{-}C_6H_4\text{-}\underset{NH-C_6H_5}{CH}\text{-}\overset{O}{P}(OC_2H_5)_2$	150	76.6	8.4; 8.70	8.59
3	 $p\text{-}CH_3C_6H_4\text{-}\underset{NH-C_6H_5}{CH}\text{-}\overset{O}{P}(OCH_3)_2$	121-122	77.8	10.40; 10.41	10.16
4	 $p\text{-}CH_3C_6H_4\text{-}\underset{NH-C_6H_5}{CH}\text{-}\overset{O}{P}(OC_2H_5)_2$	66	82.3	9.51; 9.62	9.31
5	 $o\text{-}NO_2C_6H_4\text{-}\underset{NH-C_6H_5}{CH}\text{-}\overset{O}{P}(OCH_3)_2$	175.5-176	77.2	9.57	9.22
6	 $o\text{-}NO_2C_6H_4\text{-}\underset{NH-C_6H_5}{CH}\text{-}\overset{O}{P}(OC_2H_5)_2$	155	87.7	8.41	8.51
7	 $m\text{-}NO_2C_6H_4\text{-}\underset{NH-C_6H_5}{CH}\text{-}\overset{O}{P}(OCH_3)_2$	130-131	82.8	9.67	9.22
8	 $m\text{-}NO_2C_6H_4\text{-}\underset{NH-C_6H_5}{CH}\text{-}\overset{O}{P}(OC_2H_5)_2$	93-94	90.9	8.64	8.51

and acetophenone, propiophenone, and benzophenone, acetophenone-m-toluidine anil, and acetophenone-o-toluidine anil. The reactions were carried out in presence of sodium ethoxide and with application of heat, for they went either slowly or not at all in the cold. However, only the addition products with acetophenone anil and propiophenone anil were obtained in crystalline form: in the remaining cases the products were thick syrups that did not crystallize on standing. The melting points and yields of the products obtained are given in Table 3.

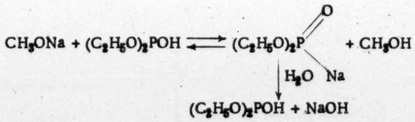
We carried out also experiments on the addition of diethylphosphorous acid to benzylidenephenylhydrazine and certain of its derivatives, but in spite of long heating of the reaction mixture at 200°, the reaction did not go: only starting materials were isolated.

Finally, in view of the great variation in the ability of different anils to combine with diethylphosphorous acid, we decided to make a kinetic study of these reactions; in particular, we considered that it was of great interest to determine the effects of substituents in the benzene nuclei of the anils on the rate of dialkylphosphorous acid addition. We chose, as our first subject for investigation, the reaction between benzylideneaniline and diethylphosphorous acid. Concentrations of 0.725 – 1.45 mole/liter were employed, and a 17.4% solution of sodium methoxide in absolute methanol was used as catalyst; the reaction was carried out in a thermostat at temperatures

TABLE 2

No.	Formula	B.p. °C	Yield %	Phosphorus (%)	
				found	calculated
1	 $C_6H_5-\underset{P(=O)(OC_2H_5)_2}{CH}-NH-C_6H_4Cl-(p)$	111-113	75.4	8.89	8.78
2	 $(m)-NO_2-C_6H_4-\underset{P(=O)(OC_2H_5)_2}{CH}-NH-C_6H_4CH_3-(m)$	129-130	78.7	8.51	8.20
3	 $(p)-[(CH_3)_2CH]-C_6H_4-\underset{P(=O)(OC_2H_5)_2}{CH}-NH-C_6H_4Cl-(p)$	119-119.5	82.7	7.93; 7.65	7.77
4	 $(p)-CH_3-C_6H_4-\underset{P(=O)(OC_2H_5)_2}{CH}-NH-C_6H_4-CH_3-(m)$	102-103	88.0	8.90	8.90
5	 $(p)-[(CH_3)_2-CH]-C_6H_4-\underset{P(=O)(OC_2H_5)_2}{CH}-C_6H_4-CH_3-(o)$	115	79.1	8.66	8.94

varying from that of the room to 70°. The course of the reaction was followed by titrating unchanged diethylphosphorous acid with 0.5 N caustic soda in presence of phenolphthalein. The first series of experiments, in which the alcohol used as solvent was rendered absolute by treatment with lime and sodium, did not give positive results: at low concentrations of catalyst the reactions did not go, and at high concentrations they went with evolution of much heat and were practically complete in a few seconds. It is evident that traces of water, present in the alcohol, had an effect on the reaction: decomposition occurred of the sodium diethylphosphite formed:



$$\begin{array}{c} CH_3ONa + (C_2H_5O)_2POH \rightleftarrows (C_2H_5O)_2P(=O)Na + CH_3OH \\ \downarrow H_2O \\ (C_2H_5O)_2POH + NaOH \end{array}$$

In succeeding experiments we therefore used alcohol that had been rendered absolute over sodium and then magnesium. Fig. 1 presents the results of experiments carried out with a 1.45 M solution of the reactants at 50° (total volume of reaction mixture, 50 ml). Curve I was obtained by the use of 0.5 ml of sodium methoxide solution, Curve II by the use of 1.0 ml, and Curve III, which coincides with the ordinate axis, by the use of 3.0 ml.

Similar results were obtained also when 0.725 M solutions were used at 30.4° (Fig. 2): Curve I, 2 ml; Curve II, 2.5 ml; and Curve III, 3 ml of sodium methoxide solution. As before, Curve III is practically coincident with the ordinate axis.

From these experiments the conclusion may be drawn that the addition reactions of dialkylphosphorous acids to benzylideneaniline are very sensitive to moisture. We have noted this on several occasions in the addition of dialkylphosphorous acids to other unsaturated compounds. At catalyst concentrations that ensure the formation in the reaction mixture of a sufficient amount of sodium diethylphosphite, the reaction goes extremely rapidly, being practically complete in a few seconds, and is accompanied by the generation of much heat. The specific course of these reactions can, in our opinion, be explained only by the assumption that they proceed by a chain mechanism, according to the scheme:

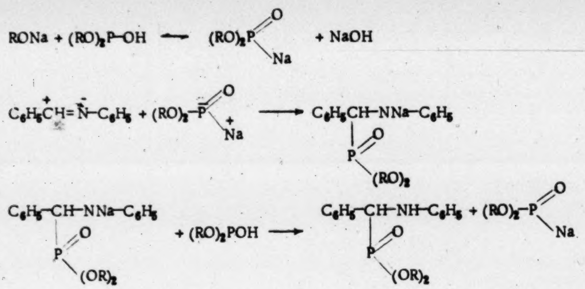
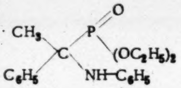
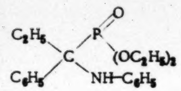


TABLE 3

No.	Formula	B.p. °C	Yield %	Phosphorus (%) found	Phosphorus (%) calculated
1		106-108	75	9.40	9.30
2		119-120	78.8	9.13	8.91

EXPERIMENTAL

General Procedure in Addition Reactions of Dialkylphosphorous Acids with Benzylideneaniline Derivatives

A saturated solution of sodium alkoxide in alcohol (15-20 drops) was added to a mixture of the benzylideneaniline derivative (3-4 g), an equimolecular amount of the dialkylphosphorous acid, and some absolute alcohol (a few milliliters, required to dissolve the anil). In order to avoid radical exchange, in the course of the reaction, between the dialkylphosphorous acid and the alkoxide, these reagents were chosen so as to have identical radicals. The reactions were generally accompanied by appreciable generation of heat. When the catalyst had been added, the reaction mixture was heated on a water bath for one hour and was then poured out into a porcelain dish. Depending on the nature of the anil used, crystallization began either immediately on cooling, or after several hours, or after several days. In a number of cases a crystalline product was not obtained even after a long period of standing. The crystalline products were filtered off, washed with cold alcohol, and recrystallized several times from hot ethanol until a constant melting point was obtained.

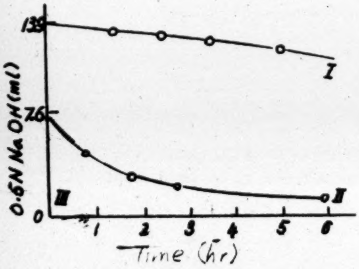


Fig. 1

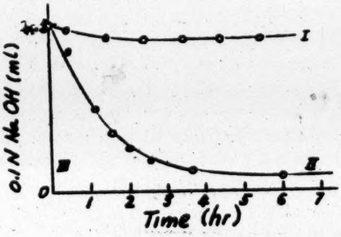


Fig. 2

Addition of Dialkylphosphorous Acids to Acetophenone Anil and its Derivatives

A saturated solution of sodium alkoxide (25-25 drops was added to a mixture of the ketone anil (3-4 g) and an equimolecular amount of the dialkylphosphorous acid. In most of the experiments the reaction mixture did not become warm. It was heated on a bath having a temperature of 150-180° for 1-2 hours, and was poured, after cooling, into a porcelain dish containing a few milliliters of alcohol. The crystalline products obtained were recrystallized from hot ethanol.

Kinetics of the Addition of Diethylphosphorous Acid to Benzylideneaniline

1. Diethylphosphorous acid in aqueous-alcoholic solution was titrated with 0.5 N NaOH in presence of phenolphthalein: 1 g of diethylphosphorous acid required 14.4 ml of 0.5 N NaOH (theory requires 14.5 ml). It was concluded that it was possible to determine the amount of unchanged diethylphosphorous acid present during the addition reaction by titration with caustic soda solution.

2. The procedure used in the kinetic studies was as follows: The benzylideneaniline was introduced into a 50-ml measuring flask, an equimolecular amount of diethylphosphorous acid was added, and absolute ethanol was added to a volume of 40-45 ml. The flask was placed in a thermostat, and after 30 minutes a solution of sodium methoxide was added, after which the contents of the flask were made up to volume by addition of absolute ethanol that had been heated in the thermostat. Analysis was carried out by transferring 5-ml portions to conical flasks containing a water-alcohol mixture; the unchanged diethylphosphorous acid was titrated rapidly with a 0.5 N or 0.1 N solution of NaOH. A "blank" experiment was carried out simultaneously. For illustration purposes we will give the results of one determination (Fig. 1). Benzylideneaniline, 13.1 g; diethylphosphorous acid, 10.0 g; 17.6% methanolic solution of sodium methoxide, 0.5, 1.0, and 3.0 ml. Temperature 50°. Blank experiment: 5 ml of solution required 13.9 ml of NaOH solution.

TABLE 4

No.	Time since beginning of expt.(hr)	0.5 N NaOH used in titration of diethylphosphorous acid (ml)		
		0.5 ml of catalyst	1.0 ml of catalyst	3 ml of catalyst
1	0	13.9	7.6	0
2	0.75	–	4.4	–
3	1.50	13.0	–	–
4	1.75	–	3.0	–
5	2.50	12.6	–	–
6	2.75	–	2.3	–
7	3.50	12.4	–	–
	5.00	9.5	–	–
	24.00	9.3	1.4	–

SUMMARY

A new method has been developed for the synthesis of amino phosphonics acids. It consists in the addition of dialkylphosphorous acids to anils in presence of alkali-metal alkoxides.

Received June 23, 1952

V.I. Ulyanov Lenin
Kazan State University

LITERATURE CITED

[1] E. Knoevenagel, Ber. 37, 4081 (1907); P. Petrenko-Kritschenko, Ber. 42, 3683 (1909); E. Beckman, Ber. 23, 3340 (1890); R. Schiff, Ber. 31, 607, 206, 1390 (1898); K. Garzorolli, Ber. 32, 2277 (1899); M. Busch, Ber. 37, 2691 (1904).

[2] A. N. Pudovik, Proc. Acad. Sci. USSR., 73, 499, 327 (1950); 80, 65 (1951); Bull. Acad. Sci. U.S.S.R. Div. Chem. Sci., No. 5, 522 (194[illegible]); J. Gen. Chem., 21, 383, 1837 (1951)*. A. N. Pudovik, ibid. 22, 462, 467, 473 (1952)**

[3] A. N. Pudovik, Proc. Acad. Sci. USSR 83, 865 (1952).

[4] A. N. Pudovik, Proc. Acad. Sci. USSR 73, 327, 499 (1950).

---

* See Consultants Bureau translation, p. 423, 2035

** See Consultants Bureau translation, p. 525, 531, 537.

BLANK
PAGE

ADDITION OF DIALKYLPHOSPHOROUS ACIDS AND OF THEIR ACID CHLORIDES TO α-EPOXIDES

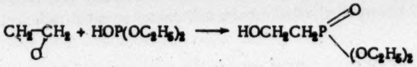
A. N. Pudovik and B. E. Ivanov

α-Epoxides form a class of very reactive organic compounds; they are capable of the most varied reactions: addition, replacement of oxygen, isomerization, and polymerization. Of these the most varied and interesting in theoretical and in practical respects are addition reactions. It has now been shown that α-epoxides are able to combine with the most varied substances: alcohols, phenols, water, organic acids and their acid chlorides, aldehydes and ketones, hydrogen halides, amino acids, malonic and acetoacetic esters, organomagnesium compounds, hydrogen sulfide and mercaptans, sulfuryl chloride, sulfuric chloride, and a number of others [1].

In connection with the work that one of us has been carrying out in recent years on the addition of dialkylphosphorous, dialkylphosphorothious, and alkyl- and aryl-phosphonous acids to unsaturated compounds [2] and of various nucleophilic reagents to vinylphosphonic esters [3], we considered it to be of interest and of importance to extend these investigations to a study of the addition of dialkylphosphorous acids, their analogs, and their acid chlorides to α-epoxides.

The addition of dialkylphosphorous acids to α-epoxides has remained practically without study until now. In the literature there is only a cursory reference to the possibility of such an addition by Chelintsev and Kuskova [4]: in the course of a reaction between ethylene oxide and sodium diethyl phosphite they obtained a syrup, in which the presence of quinquevalent phosphorus was established spectroscopically; no individual products were isolated from the mixture. We commenced our investigation by repeating Chelintsev and Kuskova's experiment. After passing ethylene oxide into an ethereal solution of sodium diethyl phosphite, treating the reaction mixture with acetic acid, filtering off sodium acetate, and distilling off the ether, we obtained a liquid similar in amount and appearance to that described by Chelintsev and Kuskova. However, vacuum fractionation indicated that it consisted essentially of diethylphosphorous acid and a small amount (several drops) of a fraction of b.p. 115-125°/5 mm; an appreciable amount of resinlike residue remained. Performance of the reaction at higher temperatures improved the yield of high-boiling fraction only slightly.

Petrov [5], in a study of the addition of alcohols to α-epoxides, has shown that a very effective catalyst in these reactions is boron trifluoride and its complexes with oxygen-containing compounds. It was of interest to examine the possibility of their application in the addition reactions of dialkylphosphorous acids, and we carried out experiments that indicated that they could be so applied: for the reaction between ethylene oxide and diethylphosphorous acid, the greatest yield (15-16%) of diethyl 2-hydroxyethylphosphonate was obtained when the reaction was carried out at 130-140° in presence of the ether complex (etherate) of boron trifluoride:



$$\underset{\diagdown O \diagup}{CH_2-CH_2} + HOP(OC_2H_5)_2 \longrightarrow HOCH_2CH_2P(=O)(OC_2H_5)_2$$

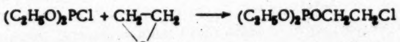
At lower temperatures (80-90°) the reaction does not go, and at higher temperatures (about 160°) the yield of addition product falls owing to formation of high-boiling fractions and resins. Addition to ethylene oxide of dimethylphosphorous acid proceeds in similar fashion, but we did not succeed in bringing about addition of dibutyl- and diisobutyl-phosphorous acids under our experimental conditions.

Since substituted α-epoxides are more reactive than ethylene oxide, we then carried out a series of experiments on the addition of diethylphosphorous acid to 1,2-epoxycyclohexane and to 1,2-epoxy-3-ethoxypropane in presence of boron trifluoride etherate; also of sodium diethyl phosphite to 1,2-epoxy-3-ethoxypropane. The addition product from 1,2-epoxycyclohexane (diethyl 2-hydroxycyclohexylphosphonate) was obtained in 20% yield. In the addition of diethylphosphorous acid to 1,2-epoxy-3-ethoxypropane, one or other of two different products, corresponding by analysis and molecular-refraction results to the diethyl ester of ethoxyhydroxypropylphosphonic acid, were obtained according as catalyst was used or not. It is evident that, as in the case of the addition of alcohols [5], the catalyst has a determining effect on the direction of addition of dialkylphosphorous acids to α-epoxides. By analogy to the corresponding alcohol reactions, it may be supposed that addition of sodium dialkyl phosphite to 1,2-epoxy-3-ethoxypropane yields the normal addition product — diethyl 3-ethoxy-2-hydroxypropylphosphonate — whereas in presence of boron trifluoride reaction is abnormal and yields diethyl 2-ethoxy-2'-hydroxyisopropylphosphonate. In neither case does the yield of addition product exceed 20%.

Addition to α-epoxides of acid chlorides derived from partial phosphorous esters were studied by Kabachnik in a series of investigations [6]: he studied the addition of diphenyl phosphorochloridite, phenyl phosphorodichloridite, and o-phenylene phosphorochloridite to ethylene oxide. In the first case he isolated 2-chloroethyl diphenyl phosphite, which was converted, when strongly heated, into a tetraphenyl ethylenediphosphonate with loss of dichloroethane (2-chloroethyl o-phenylene phosphite behaved similarly).

Mixed phosphorous esters containing only aliphatic radicals were prepared by Kabachnik and Rosiiskaya [7] by Milobendzsky's reaction from Menshutkin's acid chloride. Thus, 2-chloroethyl diethyl phosphite was synthesized from the acid chloride $ClCH_2{\cdot}CH_2OPCl_2$ and alcohol in presence of pyridine, although the yield obtained by this reaction was only about 21%. Thermal isomerization of 2-chloroethyl diethyl phosphite yielded diethyl 2-chloroethylphosphonate.

In view of the great theoretical interest afforded by mixed aliphatic esters of phosphorous acid, we decided to carry out their synthesis by the action of dialkyl phosphorochloridites on α-epoxides. Until recently, dialkyl phosphorochloridites have been inaccessible substances, but A. E. Arbuzov and coworkers have now developed a convenient method of synthesis consisting in the direct action of two molecular proportions of an alcohol on one molecular proportion of phosphorus trichloride in presence of dimethylaniline. In this way diethyl phosphorochloridite, ethylene phosphorochloridite, and a number of other cyclic phosphorochloridites have been synthesized [9]. The reaction between ethylene oxide and diethyl phosphorochloridite was very vigorous; it was carried out simply by passing gaseous ethylene oxide through the cooled phosphorochloridite. Fractionation of the reaction mixture yielded three products: 2-chloroethyl diethyl phosphite (51%), triethyl phosphite (13%), and bis(2-chloroethyl) ethyl phosphite (15%). The formation of triethyl phosphite and of bis(2-chloroethyl)ethyl phosphite can be explained by disproportionation of 2-chloroethyl diethyl phosphite during reaction:

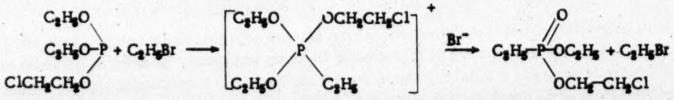


$$(C_2H_5O)_2PCl + \underset{\diagdown O \diagup}{CH_2{-}CH_2} \longrightarrow (C_2H_5O)_2POCH_2CH_2Cl$$

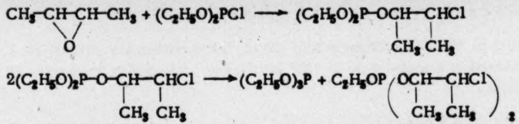
$$2(C_2H_5O)_2POCH_2CH_2Cl \longrightarrow (C_2H_5O)_3P + (C_2H_5O)P(OCH_2CH_2Cl)_2.$$

A similar phenomenon was observed by Kabachnik in the reaction between ethylene oxide and diphenyl phosphorochloridite [6].

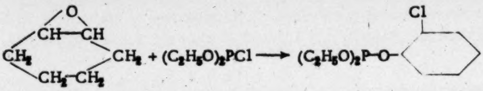
The constants of the products we have obtained are identical with those obtained for the same substances by Kabachnik . We subjected 2-chloroethyl diethyl phosphite to the isomerization reaction in presence of ethyl bromide: it was of interest to determine which of the radicals in the phosphorous ester — ethyl or 2-chloroethyl — would participate in the Arbuzov rearrangement. Experiment showed that the reaction went only in one direction, with formation of the isomerized product, 2-chloroethyl ethyl ethylphosphonate; an ethyl radical had therefore been split off.



We prepared 2,3-epoxybutane by oxidizing 2-butene with peroxyacetic acid in a dry ether medium, and its ethereal solution was applied directly in the reaction with diethyl phosphorochloridite (the reaction was carried out under cooling with ice water). Fractionation of the reaction mixture yielded three products: triethyl phosphite, 2-chloro-1-methylpropyl diethyl phosphite, and bis(2-chloro-1-methylpropyl)ethyl phosphite. The yield of 2-chloro-1-methylpropyl diethyl phosphite was 55%.

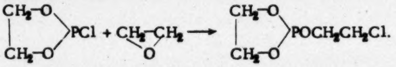


No tris(2-chloro-1-methylpropyl) phosphite was detected in the products. In the reaction between 1,2-epoxycyclohexene and diethyl phosphorochloridite, only one product was isolated: 2-chlorocyclohexyl diethyl phosphite (60%):



No high-boiling fractions were obtained.

Finally, we carried out the reaction between ethylene oxide and ethylene phosphorochloridite. The reaction was very vigorous, much heat being evolved. The only product was 2-chloroethyl ethylene phosphite, obtained in 95% yield:



The product had constants identical with those of the substance obtained by A. E. Arbuzov, Zoroastrova, and Rizpolozhensky by the action of 2-chloroethanol on ethylene phosphorochloridite in presence of pyridine.

EXPERIMENTAL

Addition of Diethylphosphorous Acid to Ethylene Oxide

Expt. 1. Finely cut sodium (1.7 g) was added to absolute ether (100 ml) contained in a flask provided with reflux condenser and dropping funnel, from which diethylphosphorous acid (10 g) was added. The mixture was allowed to stand, first at room temperature and then warm, on a water bath, until the sodium had completely dissolved. Gaseous ethylene oxide was passed through the solution until the weight had increased by 3.5 g, and then acetic acid (5.5 g) was added. The precipitate of sodium acetate was filtered off, and ether was distilled off on a water bath. The residue was fractionally distilled under 10 mm pressure, yielding:

Fraction 1, b.p. 70-80°; 8 g (diethylphosphorous acid)
Fraction II, b.p. 80-110°; a few drops
Fraction III, b.p. 110-120°; a few drops

The residue in the flask was a resinous mass containing an appreciable amount of sodium acetate.

Expt. 2. An ethereal solution of sodium diethyl phosphite, obtained as in Expt. 1, was heated at 40° on a water bath, and ethylene oxide was passed until the increase in weight attained 3.5 g. After removal of precipitate and solvent, a syruplike mass was obtained, from which by fractionation under 5 mm pressure the following three fractions were obtained:

Fraction I, b.p. 60-70°; 6 g (diethylphosphorous acid)
Fraction II, b.p. 70-120°; 1 g
Fraction III, b.p. 120-130°; 1.5 g

Expt. 3. A small amount of sodium was dissolved in diethylphosphorous acid (5 g), ethylene oxide (5 g) was added, and the mixture was sealed in a tube and heated for five hours at 60°. Fractionation showed that the reaction had not gone. A similar experiment was carried out with the same amounts of reactants, but in presence of an alcoholic solution of sodium ethoxide (3 drops); however, vacuum fractionation yielded only the original substances.

Expt. 4. A mixture of diethylphosphorous acid (13.8 g), boron trifluoride etherate (0.1 ml), and ethylene oxide (6 g) was heated in a sealed tube at 85-90° for four hours. Fractionation of the reaction mixture yielded the original substances and also a fraction (about 1 g) of b.p.130-150°/5 mm.

Expt. 5. A mixture of diethylphosphorous acid (20 g), boron trifluoride etherate (0.015 ml), and ethylene oxide (10 g) was heated in a sealed tube at 130° for 8 hours. Vacuum fractionation of the mixture yielded the following fractions:

Fraction I, b.p. 30-84° at 4.5 mm; 4 g
Fraction II, b.p. 60-70° at 4.5 mm; 8 g (diethylphosphorous acid)
Fraction III, b.p. 70-120° at 4.5 mm; 1 g
Fraction IV, b.p. 125-145° at 4.5 mm; 8 g

There was only a small amount of resinous residue in the flask. Refractionation of the fraction of b.p. 125-145°/4.5 mm yielded diethyl 2-hydroxyethylphosphonate, b.p. 122-124°/8 mm; n_D^{20} 1.4380; d_4^{20} 1.0927.

Found %: P 16.72
$C_6H_{15}O_4P$. Calculated %: P 17.02

Expt. 6. A mixture of diethylphosphorous acid (20 g), sulfuric acid (sp. gr. 1.8), and ethylene oxide (10 g) was heated at 130° for 8 hours. Fractionation of the mixture under 5 mm pressure yielded the following fractions:

Fraction I, b.p. 60-70°; 18 g (diethylphosphorous acid)
Fraction II, b.p. 70-115°; 2 g
Fraction III, b.p. 115-125°; 3 g n_D^{20} 1.4364

There was only a very small residue in the flask.

Addition of Dimethylphosphorous Acid to Ethylene Oxide

A mixture of dimethylphosphorous acid (20 g), boron trifluoride etherate (0.015 ml), and ethylene oxide (12 g) was heated in a sealed tube at 130-135° for 8 hours. Ethylene oxide was removed from the reaction mixture under suction, and vacuum fractionation then yielded 5 g of a fraction of b.p. 85-99°/6 mm. A residue of about 6 g remained in the flask. Refractionation yielded dimethyl 2-hydroxyethylphosphonate (3 g) having b.p. 95-97° at 6 mm; n_D^{20} 1.4240; d_4^{20} 1.1711; found MR_D 33.4; calculated MR_D 33.06.

Found %: P 19.83
$C_4H_{11}O_4P$. Calculated %: P 20.09

Addition of Diisobutyl- and Dibutyl-phosphorous Acids to Ethylene Oxide

Expt. 1. A mixture of dibutylphosphorous acid (10 g), ethylene oxide (6 g), and boron trifluoride etherate (0.015 ml) was heated at 130-135° for 8 hours. Fractionation of the reaction mixture yielded the original substances.

Expt. 2. A mixture of diisobutylphosphorous acid (15 g), ethylene oxide (7 g), and boron trifluoride etherate (0.015 ml) was heated at 130-135° for 8 hours. Fractionation of the reaction mixture showed that the reaction had not gone. Repetition of Expts. 1 and 2 at 160-170° again did not lead to positive results.

Addition of Diethylphosphorous Acid to 1,2-Epoxy-3-ethoxypropane

Expt. 1. Finely cut sodium (2.3 g) was added to absolute ether (100 ml), and diethylphosphorous acid (13.8 g) was added dropwise from a dropping funnel. The mixture was set aside until the sodium had completely dissolved. 1,2-epoxy-3-ethoxypropane (10.2 g) was added slowly to the ethereal solution obtained, and the reaction mixture was then heated on a water bath for three hours. Heating was discontinued, glacial acetic acid (7 g) was added, the precipitate of sodium acetate was filtered off, and the ether was driven off on a water bath. Vacuum fractionation of the residue at 5 mm yielded the following fractions:

Fraction I, b.p. 45-46°; 4 g
Fraction II, b.p. 65-115°; 0.7 g
Fraction III, b.p. 115-125°; 3.5 g

Refractionation of the fraction of b.p. 115-125°/5 mm yielded a product (1.7 g) of b.p. 115-116°/5 mm; d_4^{20} 1.0831; n_D^{20} 1.4385; found MR_D 58.1; calculated MR_D 57.8.

Found %: P 12.64
$C_9H_{21}O_5P$. Calculated %: P 12.92

Expt. 2. A mixture of diethylphosphorous acid (13.8 g), 1,2-epoxy-3-ethoxypropane (10.2 g), and boron trifluoride etherate (0.05 ml) was heated in a sealed tube at 130-135° for 8 hours. Fractionation of the reaction mixture under 5 mm pressure yielded the fractions:

Fraction I, b.p. 45-70°; 10 g
Fraction II, b.p. 70-130°; 0.8 g
Fraction III, b.p. 130-140°; 5 g
Fraction IV, b.p. 140-170°; 4.5 g

Refractionation of the fraction of b.p. 130-140°/5 mm yielded a substance (3 g) having b.p. 137-139° at 7 mm; d_4^{20} 1.1023; n_D^{20} 1.4432; found MR_D 57.64; calculated MR_D 57.8.

Found %: P 13.13; 13.07
$C_9H_{21}O_5P$. Calculated %: P 12.92

Refractionation of the fraction of b.p. 140-170°/5 mm yielded a fraction (2.5 g) having b.p. 155-156° at 7 mm; n_D^{20} 1.4520; d_4^{20} 1.1745.

Found %: P 14.88; 15.01

Addition of Diethylphosphorous Acid to 1,2-Epoxycyclohexane

A mixture of diethylphosphorous acid (25 g), 1,2-epoxycyclohexane (16 g), and boron trifluoride etherate (0.015 ml) was heated in a sealed tube at 140-150° for 8 hours. Vacuum fractionation of the reaction mixture yielded a fraction (7 g) of b.p. 140-150°/8 mm. Refractionation yielded diethyl 2-hydroxycylohexylphosphonate (4.5 g) having b.p. 142-144° at 8 mm; d_4^{20} 1.0930; n_D^{20} 1.4620; found MR_D 59.3; calculated MR_D 58.57.

Found %: P 13.09
$C_{10}H_{21}O_4P$. Calculated %: P 13.18

Addition of Diethyl Phosphorochloridite to Ethylene Oxide

Gaseous ethylene oxide was passed through diethyl phosphorochloridite (35 g) until there was an increase in weight of 10 g; the temperature of the reaction mixture was maintained in the range 20-25° by cooling the flask in ice water. Fractionation of the reaction mixture at 15 mm gave the following fractions:

Fraction I, b.p. 54- 58°; 7 g
Fraction II, b.p. 80- 89°; 25 g; n_D^{20} 1.4370
Fraction III, b.p. 89-125°; 2 g; n_D^{20} 1.4560
Fraction IV, b.p. 125-128°; 8 g; n_D^{20} 1.4609

Refractionation of Fraction I through a Widmer column yielded triethyl phosphite (4 g) of b.p. 46° at 7 mm; n_D^{20} 1.4138; d_4^{20} 0.9866. Refractionation of Fraction II yielded 2-chloroethyl diethyl phosphite (20 g) of b.p. 72-74° at 5 mm; n_D^{20} 1.4392; d_4^{20} 1.1038; found MR_D 47.89; calculated MR_D 47.84, (according to Kabachnik and Rossiiskaya, 2-chloroethyl diethyl phosphite has the constants: 71-72° at 5 mm; n_D^{20} 1.4391; d_4^{20} 1.1025. Our last fraction had constants (b.p. 125-128° at 15 mm; n_D^{20} 1.4609; d_4^{20} 1.2268) that corresponded to those of bis(2-chloroethyl)ethyl phosphite, also prepared by Kabachnik and Rossiiskaya (b.p. 111-113° at 6 mm; n_D^{20} 1.4617; d_4^{20} 1.2294).

Isomerization of 2-Chloroethyl Diethyl Phosphite.

A mixture of 2-chloroethyl diethyl phosphite (10 g) and ethyl bromide (5.5 g) was heated in a sealed tube for five hours at 160°. Vacuum fractionation yielded 2-chloroethyl ethyl ethylphosphonate (7 g) having b.p. 67-68° at 7 mm; d_4^{20} 1.0911; n_D^{20} 1.4168; found MR_D 46.19; calculated MR_D 45.64.

Found %: P15.69
$C_6H_{14}O_3ClP$. Calculated %: P 15.46

Addition of Diethyl Phosphorochloridite to 2,3-Epoxybutane

Diethyl phosphorochloridite (10 g) was added to a cooled ethereal solution of 2,3-epoxybutane. Excess of 2-butene and ether was removed under suction from a water pump, and the residue was fractionated under 12 mm through a Widmer column. Three fractions were isolated:

Fraction I, b.p. 54-56°; 3 g
Fraction II, b.p. 80-99°; 7.5 g
Fraction III, b.p. 135-140°; 4.5 g

Refractionation of Fraction I yielded triethyl phosphite (2.5 g) having b.p. 49-50° at 9 mm; n_D^{20} 1.4140. Refractionation of Fraction II yielded 2-chloro-1-methylpropyl diethyl phosphite (5 g) having b.p. 99° at 12 mm; n_D^{20} 1.4367; d_4^{20} 1.0633; found MR_D 56.3; calculated MR_D 57.08.

Found %: P 13.89
$C_8H_{18}O_3ClP$. Calculated %: P 13.57

Refractionation of Fraction III yielded bis(2-chloro-1-methylpropyl)ethyl phosphite (4 g) having b.p. 130-132° at 5 mm; n_D^{20} 1.4500; d_4^{20} 1.0931; found MR_D 71.54; calculated MR_D 71.18.

Found %: P 10.64; 10.37
$C_{10}H_{21}O_3Cl_2P$. Calculated %: P 10.65

Addition of Diethyl Phosphorochloridite to 1,2-Epoxycyclohexane

Diethyl phosphorochloridite (6.5 g) was added gradually to 1,2-epoxycyclohexane (4 g); the reaction mixture became very hot. Vacuum fractionation yielded a fraction (5 g) of b.p. 130-135°/17 mm, and from this, on refractionation, 2-chlorocyclohexyl diethyl phosphite (3 g) was obtained; it had b.p. 130-132° at 17 mm; n_D^{20} 1.4650; d_4^{20} 1.1082; found MR_D 63.38; calculated MR_D 64.11.

Found %: P 12.47
$C_{10}H_{20}O_3ClP$. Calculated %: P 12.18

Addition of Ethylene Phosphorochloridite to Ethylene oxide

Gaseous ethylene oxide was passed through cooled ethylene phosphorochloridite (15 g) until there was an increase in weight of 5.5 g. Fractionation through a Widmer column yielded 2-chloroethyl ethylene phosphite (19 g) having b.p. 82-83° at 10 mm; d_4^{20} 1.3185; n_D^{20} 1.4760. According to A.E. Arbuzov, Zoroastrova, and Rizpolozhensky it has the following constants: b.p. 78.5-79.5° at 6.5 mm; n_D^{20} 1.4755; d_0^{20} 1.3206.

SUMMARY

1. It has been shown that dimethylphosphorous and diethylphosphorous acids add to ethylene oxide, 1,2-epoxycyclohexane, and 1,2-epoxy-3-ethoxypropane in presence of small amounts of boron trifluoride etherate with formation of the corresponding esters of 2-hydroxyalkylphosphonic acids. When sulfuric acid or sodium diethyl phosphite is used as catalyst, the addition products are formed in low yield.

2. Diethyl and ethylene phosphorochloridites add readily to ethylene oxide, to 2,3-epoxybutane, and to 1,2-epoxycyclohexane. In the reaction between diethyl phosphorochloridite and ethylene oxide or 2,3-epoxybutane, the main product – 2-chloroethyl diethyl phosphite (or 2-chloro-1-methylpropyl diethyl phosphite) – was accompanied by by-products – triethyl phosphite and bis(2-chloroethyl) ethyl phosphite (or tris(2-chloro-1-methylpropyl)ethyl phosphite) – formed by a process of disproportionation during the reaction.

In the addition reactions between diethyl phosphorochloridite and 1,2-epoxycyclohexane and between ethylene phosphorochloridite and ethylene oxide, a single addition product was obtained in each case: 2-chlorocyclohexyl diethyl phosphite (66% yield) and 2-chloroethyl ethylene phosphite (95% yield).

LITERATURE CITED

[1] M. S. Malinovsky, Prog. Chem., 19, 576 (1950).

[2] A. N. Pudovik, Proc. Acad. Sci., U.S.S.R., 73, 327, 499 (1950); J. Gen. Chem. 21, 383, 1837 (1951); 22, 462, 467, 473 (1952). (See Consultants Bureau translation, J.Gen. Chem. p. 423, 2035 (1951); 525,531,537(1952)).

[3] A.N. Pudovik, Proc. Acad. Sci. U.S.S.R., 80, 65 (1951).

[4] V. V. Chelintsev and V. L. Kuskova, J. Gen. Chem., 9, 1481 (1946).

[5] A. A. Petrov, J. Gen. Chem., 10, 981 (1941); 14, 1038 (1944).

[6] M. I. Kabachnik, Bull. Acad. Sci., U.S.S.R., Div. Chem. Sci., 6, 631 (1947); M. I. Kabachnik and P.A. Rossiiskaya, Bull. Acad. Sci U.S.S.R. Div. Chem. Sci., 3, 295 (1946).

[7] M.I. Kabachnik and P.A. Rossiiskaya, Bull. Acad. Sci. U.S.S.R., 1, 95 (1948).

[8] T. Milobendzki, A. Sachnowski, C. 1918, 1. 1911.

[9] A.E. Arbuzov, V.M. Zoroastrova, and N.I. Rizpolozhensky, Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci., 2, 209 (1948).

V.I. Ulyanov-Lenin Kazan State University
Received June 23, 1952

ETHYLPHOSPHONOUS ESTERS AND SOME OF THEIR REACTIONS

COMMUNICATION 2. PARTIAL ESTERS OF ETHYLPHOSPHONOUS ACID

B. A. Arbuzov and N. I. Rizpolozhensky

On account of their interesting properties, partial esters of phosphorous acid (dialkylphosphorous acids) have been studied in some detail. Dialkylphosphorous acids now find wide application in the synthesis of organophosphorus compounds of various types: thus, their salts react with organic halides, yielding phosphonic esters [1], and, by the action of bromine on sodium diethyl phosphite, pyrophosphorous, hypophosphoric, and pyrophosphoric esters can be prepared [2].

It has been shown in our laboratory [3] that dialkylphosphorous acids will add at a double bond with formation of phosphonic esters, and Abramov [4] has shown that they will add at the carbonyl group of an unsaturated aldehyde or ketone with formation of α-hydroxy phosphonic esters.

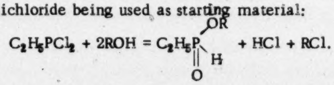
Dialkylphosphorous acids have been applied recently in the preparation of compounds of practical importance, for example, insecticides. Also, considerable attention is being devoted to the study of the structure of dialkylphosphorous acids by physical methods [5].

Unlike dialkylphosphorous acids, partial esters of alkylphosphonous acids have not been described in the literature. In structure, they are very similar to dialkylphosphorous acids, and it is therefore of great interest to study their structure and properties both by chemical and by physical methods.

In a previous communication [6] we have described some full esters of ethylphosphonous acid and a few of their reactions. In the present paper we give results on the synthesis of partial esters of ethylphosphonous acid. Levitsky [7], and later Nylen [8], proposed a method for the synthesis of dialkylphosphorous acids consisting in the treatment of phosphorus trichloride with alcohols:

$$3ROH + PCl_3 = (RO)_2POH + 2HCl + RCl.$$

This method was applied by us to the synthesis of partial esters of ethylphosphonous acid, the now accessible ethylphosphonous dichloride being used as starting material:



$$C_2H_5PCl_2 + 2ROH = C_2H_5\overset{\displaystyle OR}{\underset{\displaystyle \| \atop O}{P}}\!\diagdown_{H} + HCl + RCl.$$

A number of esters were synthesized in this way; their properties are given in the table.

EXPERIMENTAL

Apparatus and Procedure. Alkyl hydrogen phosphonites were prepared in the Arbuzov flask itself: one of the necks of the flask was stoppered, and through the cork in the other neck passed a thermometer and a dropping funnel drawn out to a capillary reaching to the bottom of the flask. The alcohol was placed in the flask, and the calculated amount of ethylphosphonous dichloride in the funnel. The delivery tube on the flask was connected to the water pump, external cooling was applied, and ethylphosphonous dichloride was sucked through the capillary at such a rate that the temperature in the flask did not rise above 0°. When the whole of the calculated amount of the ethylphosphonous dichloride had been added, the flask was allowed to stand for a further 30 minutes in the cooling mixture. Cooling was then discontinued, and hydrogen chloride was drawn off (carbon dioxide was drawn in through the capillary). When the reaction products were fractionated, the temperature of the bath was raised slowly, so that the pressure did not rise above 25 mm.

1. Methyl Hydrogen Ethylphosphonite. The materials taken for reaction were ethylphosphonous dichloride (14 g) and methanol (10.5 g) (molar ratio of 1:3). Vacuum-fractionation of the reaction products yielded:

TABLE

No.	Formula	B.p. (°C)	Pressure (mm Hg)	d_4^{20}	n_D^{20}	MR_D		Yield (%)
						Calc.	Found	
1	$C_2H_5P(OCH_3)(OH)$	65-66	11	1.0796	1.4273	25.28	25.82	19.9
2	$C_2H_5P(OC_2H_5)(OH)$	68-69	9	1.0197	1.4242	29.90	30.52	31.0
3	$C_2H_5P(OC_3H_7\text{-n})(OH)$	81-82	10	0.9937	1.4280	34.51	35.18	47.0
4	$C_2H_5P(OC_3H_7\text{-i})(OH)$	69-70	10	0.9822	1.4233	34.51	35.34	42.0
5	$C_2H_5P(OC_4H_9\text{-n})(OH)$	92-93	9	0.9759	1.4311	39.13	39.79	57.0
6	$C_2H_5P(OC_4H_9\text{-i})(OH)$	86-87	9	0.9688	1.4300	39.13	40.00	56.5
7	$C_2H_5P(OC_6H_{13}\text{-n})(OH)$	87-88	1.5	0.9511	1.4374	48.27	49.18	53.7
8	$C_2H_5P(OC_7H_{15}\text{-n})(OH)$	99-100	4	0.9386	1.4395	52.89	54.02	42.0
9	$C_2H_5P(OC_8H_{17}\text{-n})(OH)$	102-103	1	0.9320	1.4440	57.50	58.79	52.0
10	$C_2H_5P(OC_9H_{19}\text{-n})(OH)$	122-123	4	0.9230	1.4431	62.12	63.32	59.0
11	$C_2H_5P(OC_{10}H_{21}\text{-n})(OH)$	129-130	1.5	0.9296	1.4458	66.74	67.19	49.1

Frac. I, b.p. to 60° at 13-11 mm; 1.6 g
Frac. II, b.p. 60-68° at 11 mm; 4.6 g
The residue (4 g) was an almost colorless, viscous liquid.

Refractionation yielded methyl hydrogen ethylphosphonite (2.0 g, (19.9%) having the following constants: b.p. 65-66° at 11 mm; d_4^{20} 1.0796; n_D^{20} 1.4273; found MR_D 25.82; calculated for $C_3H_9O_2P$ MR_D 25.28.

Found %: P 28.52; 28.6
$C_3H_9O_2P$. Calculated %: P 28.85

Methyl hydrogen ethylphosphonite is a colorless, mobile, evil-smelling liquid.

2. Ethyl Hydrogen Ethylphosphonite. Ethylphosphonous dichloride (21.5 g) and ethanol (20.3 g) were taken for reaction. Fractionation of the reaction products yielded:

Frac. I, b.p. 40-80° at 25-11 mm; 16.5 g
The residue (8.5 g) was a colorless viscous liquid.

Refractionation yielded ethyl hydrogen ethylphosphonite (6.2 g, 31%) having the constants: b.p. 68-69° at 9 mm; d_4^{20} 1.0197; n_D^{20} 1.4242; found MR_D 30.52; calculated for $C_4H_{11}O_2P$, MR_D 29.90.

Found %: P 25.2; 25.31
$C_4H_{11}O_2P$. Calculated %: P 25.4

It is a colorless, mobile, evil-smelling liquid.

3. Propyl Hydrogen Ethylphosphonite. Ethylphosphonous dichloride (13 g) and propyl alcohol (17.8 g) were taken for reaction. Vacuum fractionation yielded:

Frac. I, b.p. to 76° at 20-15 mm; 2 g
Frac. II, b.p. 76-84° at 15-10 mm; 13 g
Residue 1.5 g

Refractionation yielded propyl hydrogen ethylphosphonite (5.8 g, 47%) having the following constants: b.p. 81-82° at 10 mm; d_4^{20} 0.9937; n_D^{20} 1.4280; found MR_D 35.18; calculated for $C_5H_{13}O_2P$, MR_D 34.51.

Found %: P 22.61; 22.60
$C_5H_{13}O_2P$. Calculated %: P 22.8

It is a colorless liquid having an unpleasant odor.

4. Isopropyl Hydrogen Ethylphosphonite. This was prepared from isopropyl alcohol (16.5 g) and ethylphosphonous dichloride (12 g). Fractionation yielded:

Frac. I, b.p. to 68° at 20-10 mm; 1.8 g
Frac. II, b.p. 69-73° at 10 mm; 10.5 g
Residue 1.6 g

Refractionation yielded isopropyl hydrogen ethylphosphonite (5.3 g, 42%) having the following constants: b.p. 69-70° at 10 mm; d_4^{20} 0.9822; n_D^{20} 1.4233; found MR_D 35.34; calculated for $C_5H_{13}O_2P$, MR_D 34.51.

Found %: P 22.6; 22.52
$C_5H_{13}O_2P$. Calculated %: P 22.8

It is a liquid having an unpleasant, phosphinelike odor.

5. Butyl Hydrogen Ethylphosphonite. This was prepared from ethylphosphonous dichloride (16 g) and butyl alcohol (27 g). Vacuum fractionation yielded:

Frac. I, b.p. 68-98° at 12-9 mm; 20 g
Residue 1.7 g

Refractionation yielded butyl hydrogen ethylphosphonite (10.5 g, 57%) having the following constants: b.p. 92-93° at 9 mm; d_4^{20} 0.9759; n_D^{20} 1.4311; found MR_D 39.79; calculated for $C_6H_{15}O_2P$, MR_D 39.13.

Found %: P 20.6; 20.65
$C_6H_{15}O_2P$. Calculated %: P 20.63

It is a colorless liquid of unpleasant phosphinelike odor, nonwetting to glass.

6. Isobutyl Hydrogen Ethylphosphonite. This was prepared from ethylphosphonous dichloride (8 g) and isobutyl alcohol (13 g). Fractionation of the reaction yielded:

Frac. I, b.p. to 85° at 20-10 mm; 3 g
Frac. II, b.p. 85-90° at 9 mm; 8.5 g
Residue 0.4 g

Refractionation yielded isobutyl hydrogen ethylphosphonite (5.2 g, 56.5%) having the following constants: b.p. 86-87° at 9 mm; d_4^{20} 0.9688; n_D^{20} 1.4300; found MR_D 40.00; calculated for $C_6H_{15}O_2P$, MR_D 39.13.

Found %: P 20.68; 20.52
$C_6H_{15}O_2P$. Calculated %: P 20.63

It is a colorless mobile liquid of unpleasant, phosphinelike odor.

7. Hexyl Hydrogen Ethylphosphonite. This was prepared from ethylphosphonous dichloride (8 g) and hexyl alcohol (19 g). Fractionation of the reaction products yielded:

Frac. I, b.p. to 117° at 15-9 mm
Frac. II, b.p. 65-87° at 1 mm; 10 g
Residue 1.2 g

Refractionation yielded hexyl hydrogen ethylphosphonite (5.8 g, 63.7%) having the following constants: b.p. 87-88° at 1.5 mm; d_4^{20} 0.9511; n_D^{20} 1.4374; found MR_D 49.18; calculated for $C_8H_{19}O_2P$, MR_D 48.27.

Found %: P 17.24; 17.3
$C_8H_{19}O_2P$. Calculated %: P 17.41

It is a mobile liquid of unpleasant phosphinelike odor; it is nonwetting to glass.

8. Heptyl Hydrogen Ethylphosphonite. This was prepared from ethylphosphonous dichloride (8.5 g) and heptyl alcohol (22.6 g). Vacuum distillation of the reaction products yielded:

Frac. I, b.p. 40-65° at 11 mm;
Frac. II, b.p. 54-96° at 4 mm;
Frac. III, b.p. 96-105° at 4 mm; 9.5 g
Residue 0.7 g

Refractionation yielded heptyl hydrogen ethylphosphonite (5.2 g, 42%) having the following constants: b.p. 99-100° at 4 mm; d_4^{20} 0.9386; n_D^{20} 1.4395; found MR_D 54.02; calculated for $C_9H_{21}O_2P$, MR_D 52.89.

Found %: P 15.85; 15.76
$C_9H_{21}O_2P$. Calculated %: P 16.12

It is a colorless mobile liquid of unpleasant, phosphinelike odor; it is nonwetting to glass.

9. Octyl Hydrogen Ethylphosphonite. This was prepared from ethylphosphonous dichloride (6.5 g) and octyl alcohol (16 g). Distillation of the reaction products yielded:

Frac. I, b.p. 63-70° at 9 mm
Frac. II, b.p. to 100° at 1.5 mm
Frac. III, b.p. 100-107° at 1.5 mm
Residue 0.6 g

Refractionation under reduced pressure yielded octyl hydrogen ethylphosphonite (5.3 g, 52.1%) having the following constants: b.p. 102-103° at 1 mm; d_4^{20} 0.9320; n_D^{20} 1.4440; found MR_D 58.79; calculated for $C_{10}H_{23}O_2P$. MR_D 57.50.

Found %: P 15.61; 15.55
$C_{10}H_{23}O_2P$. Calculated %: P 15.4

It is a colorless, mobile liquid of unpleasant odor.

10. Nonyl Hydrogen Ethylphosphonite. This was prepared from ethylphosphonous dichloride (11.5 g) and nonyl alcohol (25.5 g). Distillation of the reaction products yielded:

Frac. I, 64-120° at 3.5 mm;
Frac. II, 120-125° at 3.5 mm; 12 g
Residue 2.5 g

Refractionation yielded nonyl hydrogen ethylphosphonite (6.9 g, 59%) having the following constants: b.p. 122-123° at 4 mm; d_4^{20} 0.9230; n_D^{20} 1.4431; found MR_D 63.32; calculated for $C_{11}H_{25}O_2P$. MR_D 62.12.

Found %: P 13.78; 13.82
$C_{11}H_{25}O_2P$. Calculated %: P 14.08

It is a colorless, mobile, unpleasant-smelling liquid nonwetting to glass.

11. Decyl Hydrogen Ethylphosphonite. This was prepared from ethylphosphonous dichloride (9.3 g) and decyl alcohol (22.5 g). Distillation of the reaction products yielded:

Frac. I, b.p. 75-127° at 3 mm; 11.6 g
Frac. II, b.p. 127-129° at 3 mm; } 11.2 g
Frac. III, b.p. 129-133° at 3 mm; }
Residue 1.7 g

Refractionation yielded decyl hydrogen ethylphosphonite (8.2 g, 49.1%) having the following constants: b.p. 129-130° at 1.5 mm; d_4^{20} 0.9296; n_D^{20} 1.4458; found MR_D 67.19; calculated for $C_{12}H_{27}O_2P$; MR_D 66.74.

Found %: P 13.4; 13.45
$C_{12}H_{27}O_2P$. Calculated %: P 13.22

It is a colorless mobile liquid of unpleasant odor.

SUMMARY

1. Partial esters of ethylphosphonous acid have been synthesized by the action of alcohols on ethylphosphonous dichloride.

2. Methyl, ethyl, propyl, isopropyl, butyl, isobutyl, hexyl, heptyl, octyl, nonyl, and decyl hydrogen ethylphosphonites have been prepared.

LITERATURE CITED

[1] M. Becker, Ber. 30, 1003 (1897). [2] A. E. Arbuzov and B. A. Arbuzov, J. Gen. Chem., 2, 371 (1932). [3] A. N. Pudovik and B. A. Arbuzov, Proc. Acad. Sci. U.S.S.R., 73, 2, 327 (1950); A.N. Pudovik and B.A. Arbuzov, J. Gen. Chem., 21, 383 (1951)*; A. N. Pudovik and B. A. Arbuzov, J. Gen. Chem., 21, 1837 (1951)** [4] V.S. Abramov, Proc. Acad. Sci. U.S.S.R. 73,3,487 (1950). [5] B.A. Arbuzov and V.S. Vinogradova, Proc. Acad. Sci., U.S.S.R., 54, 9, 795 (1946); B.A. Arbuzov and V. S. Vinogradova, Proc. Acad. Sci., U.S.S.R. 55, 1, 31 (1947); B.A. Arbuzov and V.S. Vinogradova, Proc. Acad. Sci. U.S.S.R. 72, 4, 695 (1950). [6] B.A. Arbuzov and N.I. Rizpolozhensky, Proc. Acad. Sci. U.S.S.R. 83, 4, 581 (1952). [7] N. Levitsky, J. Russ. Phys.-Chem. Soc., 35, 215 (1903). [8] P. Nylen, Studien über organische Phosphorverbindungen, Upsala, 1930.

Received June 23, 1952

A. E. Arbuzov Chemical Institute
of the Kazan Affiliated Institute
of the U.S.S.R. Academy of Sciences

---

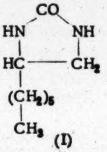
* See Consultants Bureau translation, p. 423.
** See Consultants Bureau translation, p. 2035.

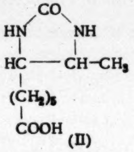
THE CURTIUS REACTION IN THE β-AMINO ACID SERIES

V. M. Rodionov and N. N. Bezinger

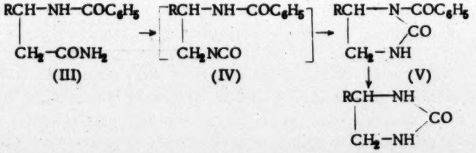
In the study of various reactions of β-amino acids, the readiness with which they are converted into various heterocyclic compounds is of great importance. In our laboratory we have now studied methods for the conversion of β-amino acids into tetra- and hexa-hydropyrimidines and into compounds of the imidazole series, and we have begun a study of syntheses of N-arylquinoline derivatives (via β-amino acids).

The conversion of β-amino acids into substituted imidazolidones is of exceptional interest, for preliminary investigations indicate that some of these compounds possess biotin activity. Thus, 4-hexyl-2-imidazolidone (I), which has been synthesized by Zvorykina [1], is very similar in structure to desthiobiotin (II) and, according to Meisel [2], differs very little from the latter in biological activity:


(I)


(II)

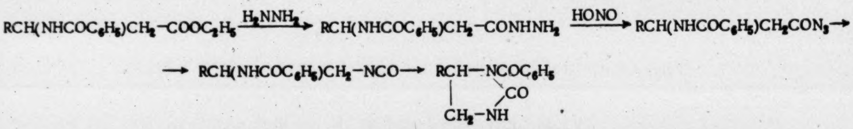
The hexylimidazolidone was prepared by the Hofmann reaction from β-benzamidopelargonamide and sodium hypobromite. The work of Zvorykina has afforded unequivocal evidence that for amides of acylated β-amino acids the Hofmann reaction proceed via the isocyanate, which undergoes intramolecular rearrangement with formation of imidazolidones containing an acyl group:



The mechanism of this reaction has been verified for a number of amides of acylated β-amino acids, and in all cases it has been confirmed by the isolation of acylated derivatives of imidazolidone (V) [3]. Whether these are isolated depends very much on the reaction temperature and on the amount of alkali. When the temperature is raised or the amount of alkali is increased, hydrolysis of (V) to give (I) is facilitated and no acylated imidazolidone can be isolated; this is what occurred in the older investigations on amides of β-amino acids.

Although this mechanism, which has been established for the formation of acyl derivatives of imidazolidone, was not in doubt, it was considered, nevertheless, that it would be very interesting to synthesize these compounds by an application of the Curtius reaction, for in that case the preparation of the isocyanates could be carried out via isolable azides. When acylamido azides are heated in an organic solvent in absence of alkali, the splitting off of the acyl group cannot occur, and the yield of acylated imidazolidones should be considerably greater than in the Hofmann reaction, which is carried out in an alkaline medium, i.e., with inevitable partial or complete splitting off of the acyl group. This supposition was fully justified, and a method has been developed for the synthesis of acylated imidazolidones.

We decided to investigate the following substances: N-benzoyl-β-phenyl-β-alanine, N-benzoyl-β-(m-nitrophenyl)-β-alanine, and N-benzoyl-β-piperonyl-β-alanine. As is well known, the Curtius reaction proceeds through the following stages: hydrazide, azide, isocyanate, and the corresponding amine. In our case the isocyanate formed underwent intramolecular rearrangement and was converted into an acylated imidazolidone:



$$RCH(NHCOC_6H_5)CH_2{-}COOC_2H_5 \xrightarrow{H_2NNH_2} RCH(NHCOC_6H_5)CH_2{-}CONHNH_2 \xrightarrow{HONO} RCH(NHCOC_6H_5)CH_2CON_3 \rightarrow$$

$$\rightarrow RCH(NHCOC_6H_5)CH_2{-}NCO \rightarrow \begin{array}{l} RCH{-}NCOC_6H_5 \\ \;|\qquad\;\; \searrow CO \\ CH_2{-}NH \nearrow \end{array}$$

The hydrazides were prepared from esters of N-benzoylated β-amino acids. The esters were boiled with a small excess of hydrazine hydrate, yielding hydrazides in 70-80% yield. The ester of N-benzoyl-β-piperonyl-β-alanine was an exception: it was found necessary to add a three-fold excess of hydrazine hydrate in this case, for otherwise the reaction did not go and the ester was isolated unchanged. An interesting observation was made when the ester of N-benzoyl-β-(m-nitrophenyl)-β-alanine was treated with a large excess of hydrazine hydrate: reaction occurred with simultaneous reduction of the nitro group and formation in good yield of the hydrazide of β-(m-aminophenyl)-N-benzoyl-β-alanine.

Two methods were tried for the preparation of azides: via the hydrazide, which was treated with oxides of nitrogen or nitrite, and by condensation of the acid chloride with sodium azide. The first method was preferred, for the azides were prepared via hydrazides in 90-95% yield and could be readily isolated in the pure state. The condensation of the acid chlorides was very slow, and very variable yields were obtained: it is possible that the lack of success was due to the use of insufficiently pure sodium azide.

When attempts were made to convert the azides into urethans, it was found that only the azide of N-benzoyl-β-phenyl-β-alanine was converted into the corresponding urethan when heated with absolute alcohol. The azides of N-benzoyl-β-(m-nitrophenyl)-β-alanine and of N-benzoyl-β-piperonyl-β-alanine did not form urethans; cyclization occurred with formation of 4-aryl-3-benzoyl-2-imidazolidones. Formationof the imidazolidone derivative generally occurred quantitatively.

The three azides all form imidazolidone derivatives when heated in dry benzene. Ring closure goes so readily in the case of N-benzoyl-β-(m-nitrophenyl)-β-alanine and N-benzoyl-β-piperonyl-β-alanine that, on being boiled with absolute alcohol, they form not the corresponding urethans, but imidazolidone derivatives.

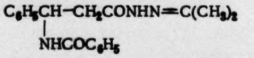
When 4-aryl-3-benzoyl-2-imidazolidones are hydrolyzed with hydrochloric acid, the ring is readily broken with evolution of carbon dioxide, splitting off of benzoic acid, and formation of the corresponding 1-arylethylenediamine. When hydrolysis is carried out with 10% caustic alkali at 80°, the benzoyl group is split off very readily, and a 4-aryl-2-imidazolidone is formed. It should be noted that in the free N-benzoyl β-amino acids, and also in their hydrazides, the benzoyl group is bound very firmly. Thus, when the hydrazides of N-benzoyl-β-phenyl-β-alanine and N-benzoyl-β-(m-nitrophenyl)-β-alanine are heated for many hours with a 10% solution of caustic alkali, the benzoyl groups are not split off. The position is similar, as already indicated, for the amides of N-benzoylated β-amino acids. We have found, therefore, that, in the Curtius rearrangement of azides of N-benzoylated β-amino acids, there are formed under our conditions five-membered cycles (imidazolidone derivatives) instead of isocyanates. The cyclization occurs extremely readily – simply by heating in an anhydrous solvent (benzene or absolute alcohol).

EXPERIMENTAL

Hydrazide of N-Benzoyl-β-phenyl-β-alanine. The ethyl ester of N-benzoyl-β-phenyl-β-alanine [4] was dissolved in 80% alcohol (100 ml), and the solution was introduced into a two-necked flask provided with reflux condenser and dropping funnel. The flask was immersed in a water bath, and the contents were heated to the boil. A solution of hydrazine hydrate (3.5 g) in water (10 ml) was added dropwise to the boiling solution, and, when the addition was complete, the reaction mixture was heated on the water bath for a further four hours. When the solution was cooled, white silky crystals of N-benzoyl-β-phenyl-β-alanine hydrazide came down; they were filtered off under suction, washed with water and then alcohol, and dried. About one half of the alcohol present was distilled off from the mother liquor, which, on cooling, yielded a further crop of hydrazide. Recrystallization from ethanol yielded 11.7 g (82% of the ester taken for reaction) of N-benzoyl-β-phenyl-β-alanine hydrazine, b.p. 212-213°.

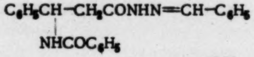
Found %: C 67.70; 67.73; H 5.59; 5.62; N 14.92; 14.70
$C_{16}H_{17}O_2N_3$. Calculated %: C 67.82; H 5.69: N 14.84

N-Benzoyl-β-phenyl-β-alanine hydrazide reduces an ammoniacal solution of silver in the cold, and Fehling's solution on being warmed. On being heated with acetone or with an alcoholic solution of benzaldehyde, it gives a high-melting condensation product, respectively:



$$\begin{array}{l} C_6H_5CH-CH_2CONHN{=}C(CH_3)_2 \\ \quad | \\ \quad NHCOC_6H_5 \end{array}$$

m.p. 221°



$$\begin{array}{l} C_6H_5CH-CH_2CONHN{=}CH-C_6H_5 \\ \quad | \\ \quad NHCOC_6H_5 \end{array}$$

m.p. 223°

N-benzoyl-β-phenyl-β-alanine hydrazide is a difficultly soluble substance, and its low solubility makes its conversion into the azide by the usual method difficult. It was thought that its hydrochloride would have a higher solubility, and an attempt was made to prepare it.

The Hydrochloride of N-Benzoyl-β-phenyl-β-alanine hydrazide. N-Benzoyl-β-phenyl-β-alanine hydrazide (4 g) was ground in a mortar with concentrated HCl (6 ml; sp. gr. 1.19). The slurry was set aside for several days in a desiccator over H_2SO_4 and alkali. The hydrochloride of N-benzoyl-β-phenyl-β-alanine was recrystallized from alcohol (4.3 g, 95.5%; m.p. 240°). The hydrochloride dissolved readily in alcohol and in hot water, but when its aqueous solutions were cooled it was almost completely precipitated, so that these solutions were not suitable for the preparation of the azide.

		C	H	N
	Found %:	C 59.96; 60.11;	H 5.34; 5.34;	N 13.00; 13.05
$C_{16}H_{18}O_2N_3Cl$	Calculated %:	C 60.07;	H 5.67;	N 13.15

N-Benzoyl-β-phenyl-β-alanyl Azide. The azide was prepared by two methods: from the hydrazide, and from N-benzoyl-β-phenyl-β-alanyl chloride.

a) Preparation of N-benzoyl-β-phenyl-β-alanyl azide from the hydrazide. Of the known methods of converting hydrazides into azides, the most convenient appeared to us to be gaseous-N_2O_3 treatment. As already mentioned, the hydrazide of N-benzoy-β-phenyl-β-alanine is difficultly soluble generally, and particularly so in water, even when acidified. The dissolution of a few grams of hydrazide requires a very large volume of water, with which it is difficult to work. The necessary N_2O_3 was obtained by addition of HNO_3 to starch.

N-benzoyl-β-phenyl-β-alanine hydrazide (5 g) was carefully ground with water (70 ml) in a mortar, and the slurry obtained was transferred to an Erlenmeyer flask, which was immersed in an ice bath. When the temperature of the slurry had reached 0°, a uniform stream of N_2O_3 (more correctly, an equimolecular mixture of NO and NO_2) was passed, care being taken that the reaction temperature did not rise above +3°. The mixture was stirred constantly and vigorously. The reaction was complete in 15-25 minutes, and it was found possible to determine accurately when the reaction was complete by a characteristic change in the appearance of the precipitate: at first this formed a homogenous mass, but towards the end of the reaction it formed into lumps and acquired a sticky appearance. When reaction was complete the azide of N-benzoyl-β-phenyl-β-alanine was extracted with ether, when all the solids present generally went into solution: if some remained undissolved, this indicated that not all of the hydrazide had reacted, in which case it could be collected and used again.

The ethereal solution of the azide was washed several times with a 3% solution of $NaHCO_3$ and then with water. It was then dried with $CaCl_2$, filtered from the $CaCl_2$, and transferred to a vessel having two side tubes. The vessel was firmly stoppered and placed in a water bath at 23-25°. A stream of dry air (dried by passage through concentrated H_2SO_4) was then passed through the solution. When the whole of the ether had evaporated, a white powder, N-benzoyl-β-phenyl-β-alanyl azide, remained in the vessel.

The azide was recrystallized from dry chloroform by dissolving it in the cold, and then partially evaporating off the solvent. The glistening crystals (4.9 g, 93.4%) that formed decomposed at 74°. N-Benzoyl-β-phenyl-β-alanyl azide dissolves readily in the cold in alcohol, ether and chloroform.

b) Preparation of N-benzoyl-β-phenyl-β-alanyl azide from N-benzoyl-β-phenyl-β-alanyl chloride and NaN_3. Dry N-benzoyl-β-phenyl-β-alanine (5 g) was heated with excess (4 ml) of thionyl chloride in a flask fitted with reflux condenser and immersed in a water bath at 40-43°. Heating was continued until bubbles of HCl ceased to be evolved from the reaction mixture (three hours), and then for a further hour (four hours in all). The excess of thionyl chloride was driven off under reduced pressure, and a brown viscous mass of pungent odor remained in the flask. On being rubbed out with absolute ether, it crystallized, forming a pale-yellow powder. N-benzoyl-β-phenyl-β-alanyl chloride was not investigated further owing to the difficulty of purifying it. Only the melting point of the impure product was determined; it was 166-168°.

The N-benzoyl-β-phenyl-β-alanyl chloride that had been prepared was transferred to an Erlenmeyer flask, and ether was added to bring the total volume to 150 ml. NaN_3 (1.4 g, i.e., 1.17 mole) was added, and the mixture was shaken mechanically for 50 hours. The ethereal solution was then separated from the precipitate, which consisted of unchanged acid chloride, NaN_3, and NaCl, and was evaporated in a stream of dry air (the vessel containing the ethereal solution was immersed in a water bath at 23-25°). The residue that remained in the vessel when the whole of the ether had been evaporated was a yellowish powder, identical in properties with the azide obtained from the hydrazide. The yield was 1.6 g (29.2% of the N-benzoyl-β-phenyl-β-alanine). Its decomposition temperature was 74°.

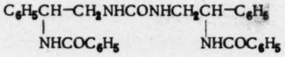
Conversion of N-Benzoyl-β-phenyl-β-alanyl Azide into the Urethan. Absolute alcohol (50 ml) was added to N-benzoyl-β-phenyl-β-alanyl azide (2 g), contained in a flask fitted with reflux condenser, and the mixture was heated on a boiling water bath for three hours. During this time there was vigorous evolution of gas (nitrogen). When reaction was complete, the solution was evaporated to dryness. A light-brown oil, which rapidly crystallized, when cooled and rubbed out, remained in the dish. The product, the ethyl ester of 2-benzamido-2-phenylethylcarbamic acid, was recrystallized from aqueous alcohol; the yield was 1.68 g (78%). The urethan melts at 163.5° and is soluble in alcohol, chloroform, acetone, and acetic acid.

Found %: C 69.39; 69.20; H 6.14; 6.17; N 8.93; 8.82
$C_{18}H_{20}O_3N_2$. Calculated %: C 69.22; H 6.45; N 8.97

Preparation of 3-Benzoyl-4-phenyl-2-imidazolidone from N-Benzoyl-β-phenyl-β-alanyl Azide. N-benzoyl-α-phenyl-β-alanyl azide (5.2 g) was placed in a flask, and absolute benzene (80 ml) was added. The mixture was maintained at the boil on a water bath; there was vigorous evolution of nitrogen. When nitrogen evolution had ceased, heating was continued for a further one hour (90 minutes altogether). The solution was cooled, and the 3-benzoyl-4-phenyl-2-imidazolidone that precipitated was filtered off and crystallized from ethanol (fine glistening needles).

Found %: C 72.20; 72.04; H 5.37; 5.50; N 10.63; 10.66
$C_{16}H_{14}O_2N_2$. Calculated %: C 72.16; H 5.30; N 10.52

Hydrolysis of 3-Benzoyl-4-phenyl-2-imidazolidone with 10% KOH. 3-Benzoyl-4-phenyl-2-imidazolidone (2.7 g) was mixed with 10% KOH solution (20 ml) and heated at 80° on the water bath for 90 minutes. The reaction mixture always contained solid material, and when heating was discontinued this was filtered off from the hot solution, washed with water and then alcohol, and dried. Recrystallization from 96% alcohol gave a light product that resembled cotton wool (0.7 g; m.p. 239.5°). Analysis indicated that the substance was probably a symmetrically dialkylated urea derivative, but it was not examined further:



$$\underset{\substack{|\\ \mathrm{NHCOC_6H_5}}}{\mathrm{C_6H_5CH}}-\mathrm{CH_2NHCONHCH_2}\underset{\substack{|\\ \mathrm{NHCOC_6H_5}}}{\mathrm{CH}}-\mathrm{C_6H_5}$$

Found %: C 73.54; 73.36; H 5.91; 6.10; N 11.16; 11.15
$C_{31}H_{30}O_3N_4$. Calculated %: C 73.94; H 5.97; N 11.06

When the alkaline filtrate was cooled, a substance separated in the form of glistening plates; it was filtered off, washed with water and then alcohol, and dried. Recrystallization from ethanol yielded a substance (0.2 g) of m.p. 162-163°. In admixture with 4-phenyl-2-imidazolidone it showed no depression of melting point.

Preparation of N-Benzoyl-β-(m-nitrophenyl)-β-alanine. β-(m-Nitrophenyl)-β-alanine (31 g) was dissolved in a 10% NaOH solution (120 ml), and the solution obtained was cooled to 0°. The solution was stirred, and benzoyl chloride (15.4 g) was added dropwise, care being taken that the temperature of the solution did not rise above +10°. When the whole of the benzoyl chloride had been added, stirring was continued for a further one hour. The solution was then acidified with HCl (1:3) until acid to Congo red. A viscous mass of N-benzoyl-β-(m-nitrophenyl)-β-alanine was precipitated. It crystallized fairly quickly and was removed from the solution, ground up, and boiled several times with water (70-100 ml) to remove the greater part of the benzoic acid present. Recrystallization from methanol gave N-benzoyl-β-(m-nitrophenyl)-β-alanine (24.5 g, i.e. 78%, based on the amount of amino acid taken for reaction) of m.p. 204-205°.

Found %: N 8.98; 8.90
$C_{16}H_{14}O_5N_2$. Calculated %: N 8.91

Preparation of the Ethyl Ester of N-Benzoyl-β-(m-nitrophenyl)-β-alanine. Concentrated H_2SO_4 (12 ml) was added cautiously to 96% ethanol (200 ml), and then N-benzoyl-β-(m-nitrophenyl)-β-alanine (21 g) was added. The mixture, contained in a flask fitted with reflux condenser, was heated on a water bath for seven hours. The whole of the N-benzoyl-β-(m-nitrophenyl)-β-alanine went into solution almost immediately. When reaction was complete, the solution was cooled and the ethyl ester of N-benzoyl-β-(m-nitrophenyl)-β-alanine came down in the form of large clear needles. It was filtered off under suction, washed with a small amount of cooled alcohol, and dried. To the stirred cooled filtrate an equal volume of water was added, and a further amount of the ester came down. It was crystallized for analysis from 70% ethanol; it had m.p. 110-110.5°. The yield was 21.0 g (92% of the N-benzoyl-β-(m-nitrophenyl)-β-alanine).

Found %: N 8.36; 8.20
$C_{18}H_{18}O_5N_2$. Calculated %: N 8.18

Preparation of N-Benzoyl-β-(m-nitrophenyl)-β-alanine Hydrazide. N-Benzoyl-β-(m-nitrophenyl)-β-alanine hydrazide was prepared by heating the ethyl ester of N-benzoyl-β-(m-nitrophenyl)-β-alanine with a slight excess of hydrazine hydrate in 70% ethanol. If the reaction is carried out in 96% ethanol with a small excess of hydrazine hydrate, the yield of hydrazide is appreciably reduced (from 70-74% to 42%). When a large excess of hydrazine hydrate is used, simultaneous reduction of the NO_2 group occurs and a mixture is obtained of the hydrazides of N-benzoyl-β-(m-nitrophenyl)-β-alanine and of β-(m-aminophenyl)-N-benzoyl-β-alanine, which cannot be separated readily by simple recrystallization.

If the reaction is carried out without solvent by heating a mixture of hydrazine hydrate (in excess) with the ethyl ester of N-benzoyl-β-(m-nitrophenyl)-β-alanine, then the hydrazide of β-(m-aminophenyl)-N-benzoyl-β-alanine is the sole product.

The ethyl ester of N-benzoyl-β-(m-nitrophenyl)-β-alanine (17.1 g; 0.05 mole) was dissolved by heat in 70% ethanol (200 ml), and hydrazine hydrate (4g; 0.08 mole) was added. The mixture, contained in a flask fitted with reflux condenser, was heated on a boiling water bath for five hours. When the solution was cooled, the hydrazide came out in a form resembling cotton wool; it was filtered off under suction, washed with alcohol, and dried. About half of the alcohol was distilled off from the filtrate, which then, when cooled, yielded a further drop of hydrazide. N-Benzoyl-β-(m-nitrophenyl)-β-alanine hydrazide [11.5 g, equivalent to 70% of the ethyl ester of N-benzoyl-β-(m-nitrophenyl)-β-alanine taken] maybe recrystallized from ethanol or methanol; m.p. 226-227°.

Found %: C 58.27; 58.75; H 4.72; 5.14; N 17.06; 16.94
$C_{16}H_{16}O_4N_4$. Calculated %: C 58.52; H 4.92; N 17.06

N-Benzoyl-β-(m-nitrophenyl)-β-alanine hydrazide is readily soluble in acids (CH_3COOH, HCl) and, when heated, in alcohol; it is completely insoluble in water. It readily reduces hot ammoniacal silver oxide and Fehling's solution.

Preparation of β-(m-aminophenyl)-N-benzoyl-β-alanine Hydrazide. Hydrazine hydrate (4.5 g; 0.09 mole) was placed in an Erlenmeyer flask fitted with reflux condenser and brought to the boil. The ethyl ester of N-benzoyl-β-(m-nitrophenyl)-β-alanine (3.4 g), was added in small portions, each portion being allowed to dissolve completely before the next was added. When the whole of the ester had been added, the solution was boiled for a further two hours and then cooled, when it formed a thick yellowish slurry. The precipitate was filtered off under suction, washed many times on the filter with water, and dried. Recrystallization from ethanol gave β-(m-aminophenyl)-N-benzoyl-β-alanine hydrazide, m.p. 205°, yield 2 g (67.2% of ethyl ester of N-benzoyl-β-(m-nitrophenyl)-β-alanine taken).

Found %: C 67.56; 67.40; H 6.10; 6.12; N 18.84; 18.72
$C_{16}H_{18}O_2N_4$. Calculated %: C 67.45; H 6.08 N 18.78

Preparation of N-Benzoyl-β-(m-nitrophenyl)-β-alanyl Azide. Water (400 ml) was added to N-benzoyl-β-(m-nitrophenyl)-β-alanine hydrazide (2 g), and the mixture was brought to the boil. The greater part of the hydrazide dissolved, and the remainder dissolved when concentrated HCl (20 ml) was added to the hot solution. The solution was cooled, suspended matter was filtered off, and the filtrate was placed in an ice bath. When the temperature of the solution had fallen to 0°, it was stirred vigorously while a solution of $NaNO_2$ (0.42 g) in water (5 ml) was added rapidly. A white flocculent precipitate came down immediately; it was rapidly filtered off under suction, washed on the filter with cold water, carefully pressed out on a porous tile, and dried in a vacuum desiccator over concentrated H_2SO_4.

N-Benzoyl-β-(m-nitrophenyl)-β-alanyl azide was recrystallized from chloroform by dissolving it in the cold and evaporating off the solvent. A small amount of crystals and a sirupy liquid remained in the dish, and to remove solvent completely the dish was placed in a vacuum desiccator for 1-2 hours. N-Benzoyl-β-(m-nitrophenyl)-β-alanyl azide remained behind in the form of glistening yellowish crystals, which decomposed at 60°. The yield of azide varied from 90 to 95% (of the equivalent of hydrazide taken).

An attempt to extract N-benzoyl-β-(m-nitrophenyl)-β-alanyl azide from the mixture obtained after addition of $NaNO_2$ by means of ether or chloroform did not lead to the required result. The azide is fairly soluble in these solvents, but it was not found possible to recover it from its solutions as such: during the standing of the solution over $CaCl_2$, splitting off of nitrogen evidently occurred with rearrangement of the azide into 3-benzoyl-4-(m-nitrophenyl)-2-imidazolidone.

Preparation of 3-Benzoyl-4-(m-nitrophenyl)-2-imidazolidone. N-Benzoyl-β-(m-nitrophenyl)-β-alanyl azide (2 g) was boiled with dry benzene (75 ml) in a flask fitted with reflux condenser. At first the azide formed into a viscous mass and floated on the surface of the benzene. Vigorous evolution of nitrogen occurred, and the viscous mass gradually resolidified, thus giving an indication of the end of the reaction. Heating was continued for a further thirty minutes (two hours altogether), the solution was cooled, and the 3-benzoyl-4-(m-nitrophenyl)-2-imidazolidone was filtered off. Recrystallization from a mixture of ethanol (five parts) and acetic acid (one part) gave fine glistening leaflike crystals (1.75 g, 96%), m.p. 233.5-234.5°.

Found %: C 61.50; 61.68; H 4.26; 4.31; N 31.51; 13.45
$C_{16}H_{13}O_4N_3$. Calculated %: C 61.72; H 4.21 N 13.49

3-Benzoyl-4-(m-nitrophenyl)-2-imidazolidone may be prepared by boiling the azide with water or alcohol. Even when the azide is boiled with absolute alcohol, the product is not the expected urethan, but 3-benzoyl-4-(m-nitrophenyl)-2-imidazolidone in 85-90% yield.

Preparation of 4-(m-nitrophenyl)-2-imidazolidone. 3-Benzoyl-4-(m-nitrophenyl)-2-imidazolidone (2 g) was mixed with 10% KOH solution (50 ml), and the mixture was heated in a flask at 80-85° on a water bath for one hour. Towards the end of this period the 3-benzoyl-4-(m-nitrophenyl)-2-imidazolidone went completely into solution. The solution was filtered hot to remove suspended matter, and was then cooled. 4-(m-Nitrophenyl)-2-imidazolidone came out in the form of a yellow powder: it was filtered off, washed with water, dried, and recrystallized from methanol. It melted at 179°.

Found %: C 52.21; 52.25; H 4.45; 4.42; N 20.40; 20.40
$C_9H_9O_3N_3$. Calculated %: C 52.17; H 4.38; N 20.32

Acidification of the alkaline filtrate with HCl (1:3) yielded benzoic acid (0.7 g).

Preparation of the Ethyl Ester of N-Benzoyl-β-piperonyl-β-alanine. N-Benzoyl-β-piperonyl-β-alanine (10 g) was dissolved in 96% ethanol, and concentrated sulfuric acid (6 ml) was added. The mixture, contained in a flask fitted with reflux condenser, was heated on a boiling water bath for seven hours. The solution was then cooled, and an equal volume of water was added. N-Benzoyl-β-piperonyl-β-alanine ethyl ester separated as a yellow mass, which crystallized almost instantaneously. It was filtered off and recrystallized from 50% ethanol (m.p. 130.5-131°), The yield was 8.95 g (82% of N-benzoyl-β-piperonyl-β-alanine taken).

Found %: N 4.26; 4.08
$C_{19}H_{19}O_5N$. Calculated %: N 4.10

Preparation of N-Benzoyl-β-piperonyl-β-alanine Hydrazide. N-Benzoyl-β-piperonyl-β-alanine ethyl ester (8 g) was dissolved by heat in 96% alcohol (100 ml), and hydrazine hydrate (3.57 g a three-fold excess) was added. The mixture, contained in a flask fitted with reflux condenser, was heated on a water bath for eight hours. When the solution was cooled, N-benzoyl-β-piperonyl-β-alanine hydrazide came down as glistening needles: it was filtered off, washed with alcohol, and dried. About two-thirds of the alcohol in the filtrate was evaporated, and by cooling the solution a further crop of the hydrazide was then obtained. N-Benzoyl-β-piperonyl-β-alanine hydrazide was recrystallized from ethanol (m.p. 224-225°). The yield was 6.9 g (90% of the ester taken for reaction).

Found %: C 62.61; 62.34; H 5.21; 5.17; N 12.91; 12.83.
$C_{17}H_{17}O_4N_3$. Calculated %: C 62.37; H 5.25; N 12.84.

N-Benzoyl-β-piperonyl-β-alanine hydrazide reduces ammoniacal silver oxide in the cold, and Fehling's solution when heated.

Preparation of N-Benzoyl-β-piperonyl-β-alanyl Azide. Boiling water (400 ml) and concentrated HCl (15 ml) were added to N-benzoyl-β-piperonyl-β-alanine hydrazide (5 g). The solution was cooled to room temperature, suspended matter present was filtered off, and the solution was cooled further to 0°. A solution of $NaNO_2$ (1.1 g) in water (5 ml) was then added rapidly under vigorous stirring. N-Benzoyl-β-piperonyl-β-alanyl azide was precipitated immediately in the form of compact white flakes: it was rapidly filtered off under suction, washed with ice water, and dried – first on a porous tile, and then in a vacuum desiccator. It decomposed at 50-51°. The yield was 4.38 g (85% of the hydrazide taken).

Preparation of 3-Benzoyl-4-piperonyl-2-imidazolidone. N-Benzoyl-β-piperonyl-β-alanyl azide (2 g) in absolute benzene (80 ml) contained in a flask fitted with reflux condenser was heated on a water bath at the boiling point of benzene. Vigorous evolution of nitrogen began at a bath temperature of about 60°, and heating was continued until evolution of nitrogen ceased (90 minutes). The solution was cooled, and the precipitated 3-benzoyl-4-piperonyl-2-imidazolidone was filtered off. It was recrystallized from butyl alcohol (m.p. 241°). The yield was 1.8 g (98%).

Found %: C 65.86; 65.91; H 4.65; 4.50; N 9.10; 8.96
$C_{17}H_{14}O_4N_2$. Calculated %: C 65.80; H 4.55; N 9.04

3-Benzoyl-4-piperonyl-2-imidazolidone is formed also when N-benzoyl-β-piperonyl-β-alanyl azide is heated with water (35-40% yield), and also when it is heated with alcohol.

Hydrolysis of 3-Benzoyl-4-piperonyl-2-imidazolidone with 10% KOH Solution. 3-Benzoyl-4-piperonyl-2-imidazolidone (2 g) was mixed with 10% KOH solution (40 ml) and heated on a water bath for one hour. An appreciable amount of solid remained in the solution throughout this time, and at the end it was filtered off from the hot solution, washed with water, and dried. The 4-piperonyl-2-imidazolidone was recrystallized from dilute alcohol (one part of alcohol and three parts of water); the melting point was 207°. When the alkaline solution was cooled, a further crop of 4-piperonyl-2-imidazolidone was obtained: the total yield was 1.24 g (93.2%). Acidification of the alkaline solution yielded benzoic acid (0.7 g).

Found %: C 58.16; 58.20; H 6.92; 6.90; N 13.60; 13.64
$C_{16}H_{16}O_3N_2$. Calculated %: C 58.24; H 6.84; N 13.58

SUMMARY

1. A general method has been developed for the preparation in good yield on N-benzoylated imidazolidone derivatives by the Curtius reaction, which is applied to esters of N-benzoylated β-amino acids.

2. The reaction has been carried out with N-benzoyl-β-phenyl-β-alanine, N-benzoyl-β-(m-nitrophenyl)-β-alanine, and N-benzoyl-β-piperonyl-β-alanine.

3. It has been found that reaction of excess of hydrazine hydrate with N-benzoyl-β-(m-nitrophenyl)-β-alanine yields the hydrazide of β-(m-aminophenyl)-N-benzoyl-β-alanine, i.e., reaction is accompanied by reduction of the nitro group.

LITERATURE CITED

[1] V.M. Rodionov and V.K. Zvorykina, Bull. Acad. Sci., U.S.S.R., Div. Chem. Sci., 3, 216, (1943).

[2] M N. Meisel, Biochem., 14, 361 (1949).

[3] V. M. Rodionov and V. V. Kiseleva, J. Gen. Chem. 18, 1906 (1948); V. M. Rodionov and B. I. Kurtev, Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci., 1, 113 (1952)•; ibid., 2,(1952)••; V. M. Rodionov and T. S. Kiseleva, Bull. Acad. Sci. U.S.S.R Div. Chem. Sci., No. 2, 278 (1952).•••

[4] V. M. Rodionov and N. N. Bezinger, Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci., 4, 696 (1952).••••

Received March 25, 1952

• See Consultants Bureau translation, p. 123.
•• " " " , p. 285.
••• " " " , p. 293.
•••• " " " , p. 637.

BLANK
PAGE

ORGANOMETALLIC "BIURET" PROTEIN COMPLEXES

K. T. Poroshin

Work on organometallic "biruet" protein complexes is acquiring ever increasing significance for the study of protein structure. Recent work of Soviet investigators [1] on the study of the copper complexes of amides and amino acids and of the organometallic "biuret" complexes of amidines and peptides has enabled the characteristic properties of these complexes to be determined and has led also to conclusions concerning their structure. Studies of "biuret" protein complexes have been made by Gavrilov, Paradashvili, and Govorov [2], by Jesserer [3], by Plekhan [4], and by others, but these investigations have suffered from a serious defect, in that casual protein preparations, not characterized by any chemical or physicochemical methods, have been taken for investigation.

The present work is concerned with spectrophotometric investigation of copper "biuret" complexes of certain proteins. The protein preparations investigated were: casein prepared according to Hammarsten, glycinin (soya bean protein), legumin (protein from peas), and gelatin. Also, we made special protein preparations, namely, so-called "proto-acids", which were isolated from vegetable and animal materials by the well known method due to Perov [5]. We investigated casein and fibrin acids and also preparations isolated from peas, oats and grain.

The characteristics of protein preparations obtained in the form of proto-acids are given in Table 1.

TABLE 1

Chemical and Physicochemical Characteristics of Protein Preparations

Characteristic	Protein preparation			
	casein	fibrin	oats	peas
Titration No.	8.35	9.3	8.09	9.10
Refractive index	1.3350	1.3348	1.3350	1.3346
Viscosity	1.30	1.53	1.40	1.71
Surface tension	0.80	0.90	0.78	0.85
Conductivity, K x 10^5	48.25	47.07	55.00	58.48
Specific rotation	−95°	−85°	−82°	−91.50°
Amine N	0.32	0.37	0.42	0.35
Total N	15.60	15.20	15.71	15.60
Amide N (% on wt.	1.62	1.75	1.80	1.90
Basic N of protein)	3.19	3.45	3.60	3.50
Monoamino-acid N	10.25	10.79	10.22	9.85

Note: A 1% solution of the protein in caustic soda was used for the physicochemical measurements. The equivalent amount of alkali, i.e., the amount necessary to convert the protein completely into proteinate, was taken: the amount required was calculated from the titration number. In the specific-rotation determination, a 1% solution of protein in 0.1 N alkali was used. The measurements were carried out at 18°.

The solutions of copper "biuret" complexes were prepared as follows. Caustic soda as a 3% solution (100 ml) was added to a 200-mg sample of the protein preparation. When the protein had dissolved, 0.25 M copper acetate was added to the alkaline solution in small portions at a time until permanent flocs of copper hydroxide remained. After one hour the precipitate of copper hydroxide, was centrifuged off, and the colored solution of the copper "biuret" complex was subjected to spectrophotometric investigation. Spectrophotometric curves were obtained with the aid of a Konig-Martens spectrophotometer. Results of spectrophotometric determinations on solutions of copper "biuret" complexes of Hammarsten casein, glycinin, legumin, and gelatine are given in Table 2.

Spectrophotomeric absorption curves for solutions of copper "biuret" complexes of these proteins are shown in Figure 1.

As will be seen from the figures given in Table 2 and from the absorption curves (Fig. 1), all of these proteins, with the exception of gelatin, have a single absorption maximum at 560 $m\mu$. The maximum for gelatin is displaced towards the longer waves (570 $m\mu$). The variation in intensity of absorption is characteristic of these preparations and points to a variation in the structure of the copper "biuret" complex for the separate components of the

TABLE 2

Values of ε* for Solutions of Copper "Biuret" Protein Complexes

Wavelength (mμ)	Hammarsten casein	Glycinin	Legumin	Gelatin
480	0.1120	0.2275	0.2130	0.2512
505	0.2315	0.2750	0.2520	0.3620
530	0.3250	0.3470	0.2980	0.4553
550	0.3760	0.3830	0.3310	0.5020
560	0.3880	0.3935	0.3487	0.5120
570	0.3712	0.3765	0.3312	0.5329
580	0.3507	0.3620	0.2768	0.5005
610	0.3015	0.3245	0.2315	0.4112
630	0.2610	0.2753	0.2248	0.3528
690	0.1468	0.1674	0.0870	0.0201
730	0.0685	0.0735	0.0129	0.0120

---

* ε is a measure of light absorption

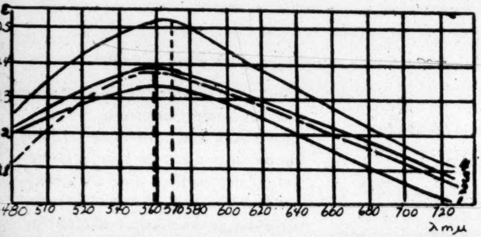


Fig. 1. Spectrophotometric absorption curves for solutions of copper "biuret" complexes of proteins. 1) Legumin; 2) Hammarsten casein; 3) glycinin; 4) gelatin.

TABLE 3

Amount of Copper Bound in "Biuret" Protein Complexes

Protein	Amount of protein (g)	Amount of copper required for formation of:				
		Complex with whole of protein (mg)	"Red" complex		"violet" tripeptide complex	
			in mg	in %	in mg	in %
Gelatin.	1.25	140.0	8.4	6.0	131.6	94.0
Legumin	1.32	187.1	9.91	5.3	177.19	94.7
Glycinin	1.35	236.5	10.1	4.24	226.4	95.75
Hammarsten casein	1.17	134.5	9.81	7.3	124.69	92.70

protein macromolecule that form so-called "red biuret complexes" with copper. In order to confirm this, the relative amounts of copper required for formation of the "red" and of the "violet" complexes were determined by the method of differential spectrophotometry that we have developed [6]. The results of the investigation are given in Table 3.

From analysis of the data in Table 3 we may conclude that the protein preparations investigated – Hammarsten casein, gelatin, and also vegetable proteins, isolated by the so-called, classical, salt method – differ from one another both in the total amount of copper required for "biuret" complex formation with the protein, and also in the relative amounts of copper required for formation of "red" (tetra-, penta-, and hexa-peptide) and "violet" (tripeptides) complexes. The amount of copper required for formation of the "red" complex is greatest for casein (7.3%); gelatin comes next (6.0%), and the vegetable proteins have still lower values: 5.3% for legumin and 4.24% for glycinin. The greater part of the protein is made up of components that give "biuret" complexes of a tripeptide character with copper, the relevant figures being: casein 92.7%, legumin 94.7%, glycinin 95.76%, and gelatin 94.0%.

The spectrophotometric investigation of these proteins was followed by a similar investigation of protein preparations isolated as "proto-acids". Solutions of their copper "biuret" complexes were prepared as for the other protein preparations. The results of spectrophotometric studies of the complexes of proteins isolated according to the method used for the preparation of casein proto-acid are given in Table 4.

The absorption curves for solutions of copper "biuret" complexes of proteins of the proto-acid type are given in Figure 2.

TABLE 4

ε-Values for Solutions of "Biuret" complexes of Proteins Isolated by the Method Used for the Preparation of Casein Proto-acid

Wavelength (mμ)	Casein	Fibrin	Pea protein	Oat-grain protein
480	0.1735	0.1552	0.1950	0.1743
505	0.2538	0.2458	0.2672	0.2457
530	0.3418	0.3310	0.3575	0.3179
550	0.4025	0.3920	0.4182	0.3743
560	0.4269	0.4115	0.4388	0.4076
570	0.4035	0.3840	0.4250	0.3790
580	0.3958	0.5720	0.4062	0.3693
610	0.3140	0.3012	0.3328	0.3005
630	0.2745	0.2507	0.2817	0.2537
690	0.1250	0.1138	0.1513	0.1230
730	0.0462	0.0430	0.0527	0.0537

From analysis of the experimental data in Table 4 and the curves in Figure 2 we may conclude that solutions of copper "biuret" complexes of protein preparations of the proto-acid type have absorption maxima at 560 mμ. The intensity of absorption is practically the same for all of the protein preparations, the greatest difference being observed at 580 mμ between pea and oats protein; the difference attains the value 0.0359. In proteins isolated by other methods, not only is there a variation in absorption maximum (gelatin 570 mμ, Hammarsten casein 560 mμ), but also a considerable variation in intensity of absorption. For example, the maximum difference in light absorption between gelatin and legumin copper "biuret" complexes at 570 mμ is 0.2007, i.e., almost ten times as great as for proteins of the proto-acid type. The curves for the proto-acids and for the so-called classical proteins are different in character.

By means of differential spectrophotometry on solutions of copper "biuret" complexes of proteins of the proto-acid type, estimations were made of the amount of copper required to form "biuret" complexes with the whole of the protein taken and also of the amounts required for formation of the red and violet components. The results are given in Table 5.

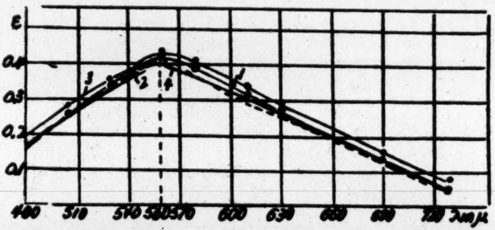


Fig. 2. Spectrophotometric absorption curves for solutions of copper "biuret" complexes of protein proto-acids: 1) casein acid; 2) fibrin acid; 3) pea protein; 4) oats protein.

TABLE 5

Amount of Copper entering into "Biuret"-Complex Formation in Proteins Isolated as Proto-acids

Protein	Amount of protein (g)	Amount of copper required for formation of:				
		Complex with whole of protein (mg)	"Red" complex		"violet" tripeptide complex	
			in mg	in %	in mg	in %
Casein acid	1.15	130.8	9.2	7.03	121.6	92.97
Oats protein	1.20	137.5	9.55	6.95	127.95	93.05
Pea protein	1.10	131.0	8.9	6.79	122.10	93.21

The results in Table 5 indicate that peptide chains containing more than three amino-acid residues comprise 6.79-7.03% of the preparation for proteins of the proto-acid type. In proteins isolated by other methods (see Table 3), the corresponding figures vary from 4.25% (glycinin) to 7.3% (Hammarsten casein). As in the case of classical proteins, the amount present as peptide chains (trimers) in the proto-acids forms the main bulk of the protein macromolecule. In proteins of the proto-acid type, the amount of copper required for formation of the violet complex comprises 92.97-93.21% of the total amount of copper entering into "biuret" complex formation. For proteins obtained by other methods (Hammarsten casein, legumin, glycinin, gelatin), the methods (Hammarsten casein, legumin, glycinin, gelatin), the corresponding amount of copper varies over a wider range, namely, 92.70%-95.75%. These figures show that the protein proto-acids comprise more homogeneous fractions than proteins prepared by other methods do.

The spectrophotometric observations on solutions of organometallic "biuret" complexes of proteins of vegetable and animal origin show that they have absorption maxima at 560 mμ. If the protein macromolecule were in the form of long polypeptide (polyamide) chains, as Fischer and Abderhalden supposed, the absorption maximum should be found at 505-520 mμ. If we accept the protein structure proposed by Zelinsky and Gavrilov [7], the structure of copper "biuret" complexes for fragments of protein microstructure may be represented as in Figures 3 and 4. We consider that the existence in the protein macromolecule of Structures 1 and 2 is confirmed by the present observations, as well as by other facts.

SUMMARY

1. Absorption-spectra curves have been obtained for solutions of the copper "biuret" complexes of vegetable and animal proteins isolated by various methods.

2. It has been shown that protein proto-acids comprise more homogeneous fractions than protein preparations obtained by other methods.

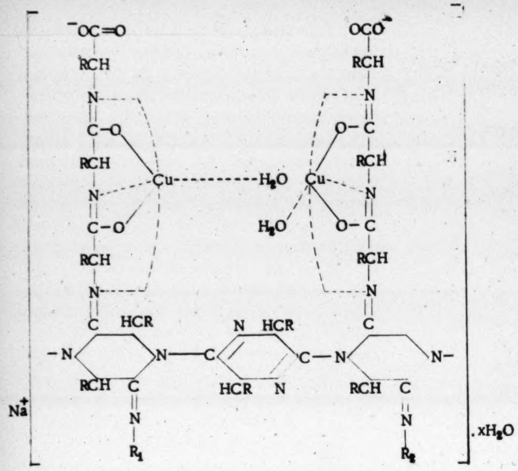


Fig. 3. Copper "biuret" protein complex, Structure 1.

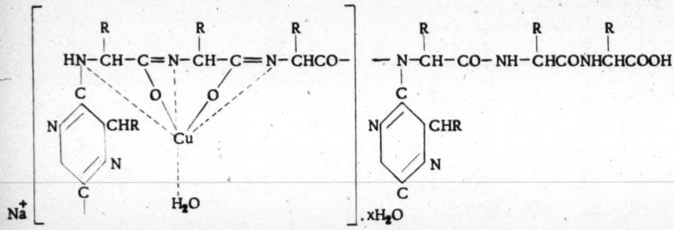


Fig. 4. Copper "biuret" protein complex, Structure 2.

3. A possible structure for the copper "biuret" complex of a microstructural protein fragment has been suggested.

Institute of Organic Chemistry of the USSR Academy of Sciences

Received April 20, 1952

LITERATURE CITED

[1] N.I.Gavrilov, M.I.Plekhan, and N.A.Poddubnaya. Bull.Acad.Sci.USSR, Div.Chem.Sci., 127 (1941); N.A. Poddubnaya and N.I.Gavrilov. J.Gen.Chem., 18, 1848,1860 (1948); M.I.Plekhan and N.I.Gavrilov. J.Gen.Chem., 18, 1843 (1948); K.T.Poroshin. Sci.Communications of Members of D.I.Mendeleev All-Union Chem.Soc., 2, 3 (1949); M.I.Plekhan. J.Gen.Chem., 21, 312, 316, 574, 579 (1951)•; Chemistry and Physical Chemistry of Macromolecular Compounds, USSR Acad.Sci.Press, Moscow (1952) 116.

[2] N.I.Gavrilov, A.A.Paradashvili, and A.I.Govorov. Biochem., 4, 35 (1939).

[3] H.Jesserer. Biochem. Ztg., 285, 36; 287; 71 (1936).

[4] M.I.Plekhan. J.Appl.Chem., 13, 620 (1940).

[5] S.S.Perov. Biochemistry of Proteins, Sov.Sci.Press (1951).

[6] K.T.Poroshin. Collected papers: Investigations on Macromolecular Compounds, USSR Acad.Sci.Press (1949), p. 193.

[7] N.D.Zelinsky and N.I.Gavrilov. Bull. Moscow State Univ., 7, 57, (1947).

• See Consultants Bureau translation, p. 341, 347, 635, 641

CATALYTIC HYDROCONDENSATION OF CARBON MONOXIDE WITH OLEFINS

COMMUNICATION 8. HYDROCONDENSATION OF CARBON MONOXIDE WITH 2-METHYLPROPENE

Ya. T. Eidus, K. V. Puzitsky, and M. I. Batuev

The reaction of catalytic hydrocondensation of carbon monoxide with olefins has now been carried out with ethylene [1-5], propene [6,7], and butene [7,8]. It was of interest to extend this reaction also to olefins having a branched carbon chain, and the present work had as its object the investigation of the hydrocondensation of carbon monoxide with a 2-methylpropene-hydrogen mixture, 2-methylpropene being taken because it is the simplest branched olefin. The apparatus and procedure were the same as in the previous investigations [2].

The 2-methylpropene used in the preparation of the initial gas mixture was obtained by dehydration over aluminum oxide of isobutyl alcohol having the following constants: b.p. 107-107.5°, d_4^{20} 0.8040; n_D^{20} 1.3954. The 2-methylpropene that was collected was fractionated, and the fraction of b.p. −6° was taken; it was completely absorbed by 63% sulfuric acid.

EXPERIMENTAL

In Table 1 results are given of experiments on an equimolecular mixture of 2-methylpropene and hydrogen containing 5-6% of carbon monoxide; the reaction was carried out at 190° and atmospheric pressure over two specially prepared catalysts, No. 42 and 43 (30 cc of each). The starting mixture had the following average composition: 45-50% 2-methylpropene, 40-45% hydrogen, and 5-6% carbon monoxide.

TABLE 1

Catalyst No.	Expt. No.	Duration of expt. (hr)	Space velocity (liter/liter.hr)	Concentration (%)	Mean yield (ml/cu. m)				Mean yield, L + H, (ml/liter.hr)	Maximum yield, L + H	
					heavy oil (H)	light oil (L)	L + H	water		(ml/cu.m)	(ml/liter.hr)
42	203	29	122	54.0	361	254	615	38	69.3	731	83.2
42	204	24	121	53.3	346	252	598	38	67.5	784	86.6
42	205	24	124	55.0	345	304	649	35	74.7	696	82.0
42	206	24	123	53.0	295	255	550	45	62.0	780	86.3
43	207	12	101	54.1	273	214	487	36	45.6	653	61.2
43	208	48	101	45.6	291	259	550	39	51.0	633	58.4
43	209	24	104	52.2	246	294	540	49	52.2	644	63.8

As will be seen from Table 1, this mixture readily undergoes the hydrocondensation reaction with formation of a liquid condensate in considerable yield. Catalyst No. 42 was particularly active: at a space velocity for the original gas of 120, the yield of condensate was, on the average, 550-650 ml/cu.m of catalyst per hour (62-69 ml/liter of catalyst per hour), and the maximum yield in the individual six-hour experiments attained 785 ml/cu. m, or 87 ml/liter. hr. Catalyst No. 42 was working for 101 hours with three regenerations (every 24 hours), and the total amount of oil (light and heavy) obtained by its aid was 206 ml. The less active catalyst, No. 43, working at a space velocity of about 100, gave an average yield of 487-556 ml/cu.m, or 45-52 ml/liter. hr; it had a working period of 84 hours, being regenerated after Expt. 207 and Expt. 208, and the total amount of oil obtained by its aid was 125 ml. These results show that the reaction rate for 2-methylpropene is not less than that of butene on Catalysts No. 29-33 [7,8].

The condensates obtained using the two catalysts were mixed. The oil was separated from water formed in the reaction and was then washed, first with caustic soda solution, and then three times with water; part of it was dried over anhydrous sodium sulfate. The dry oil had the following constants: d_4^{20} 0.6866, n_D^{20} 1.3930, and bromine number 20 (11% unsaturated hydrocarbons). Debutanization experiments showed that it contained in the dissolved condition about 5% by volume of "gas oil" (C_4).

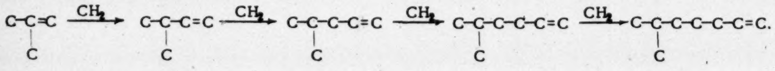
The other part of the oil (210 ml) was hydrogenated over Raney nickel (10-12%) in a half-liter autoclave at 200° at 120-130 atm for 10 hours. The hydrogenation product was filtered from the nickel and dried over anhydrous sodium sulfate; it had the following constants; d_4^{20} 0.6909; n_D^{20} 1.3964; and bromine number 2.

TABLE 2

Fraction No.	Boiling range (°C)	Vol.% of orig. oil	d_4^{20}	n_D^{20}	C_x	Hydrocarbon
1	21-28	2.7	0.6158	–	C_5	(Isopentane)
2	28-28.5	7.1	0.6196	1.3535	C_5	Isopentane
3	35-36	1.8	0.6246	1.3567	C_5	Pentane
4	49-58	0.9	0.6378	1.3648	C_6	
5	58-59	1.8	0.6502	1.3705	C_6	2-Methylpentane, 2,3-dimethylbutane (?)
6	60	14.3	0.6527	1.3710	C_6	2-Methylpentane
7	61-67	5.4	0.6603	1.3747	C_6	
8	68-89	4.0	0.6799	1.3851	C_7	
9	90-91	13.8	0.6836	1.3867	C_7	Mixture of 2-methylhexane and 3-methylhexane
10	92-113	8.0	0.6969	1.3930	$C_7 + C_8$	
11	114-118	8.0	0.7029	1.3967	C_8	2-Methylheptane
12	118-140	7.2	0.7151	1.4029	$C_8 + C_9$	
13	141-157	11.6	0.7258	1.4087	$C_9 + C_{10}$	
14	160-210	8.9	0.7473	1.4187		
15	210-291	4.5	0.7498	1.4281		
Original oil	21-291	–	0.6909	1.3964		

A part of the hydrogenated product (115 ml) was fractionated through a column of 40 theoretical plates. There was about 3 ml of gas oil, and the remaining 112 ml was separated into 13 fractions over the range 21-157° and residue; 86.6% came over below 157° (762 mm). The residue (13.3%) was distilled from a Favorsky flask. All of the fractions obtained are given with their properties in Table 2. The curve for the fractionation through the column is given in the accompanying diagram.

As will be seen from Table 2 and from the diagram, the fractions obtained in high yield correspond mainly to products formed by the lengthening of the main chain. Actually, Fraction 2 (28-28.5°; 7.1%) corresponds to 2-methylbutane, Fraction 6 (60°; 14.3%) corresponds to 2-methylpentane, Fraction 9 (90-91°; 13.8%) corresponds to 2-methylhexane, and Fraction 11 (114-118°; 8.0%) corresponds to 2-methylheptane. These results show that reaction proceeds by stepwise lengthening of a straight chain, in steps of one carbon atom:



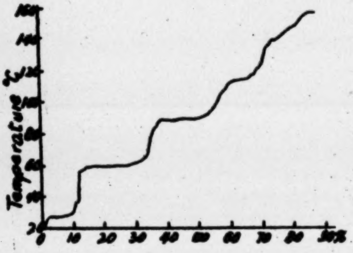
$$C-\underset{\underset{\displaystyle C}{|}}{C}=C \xrightarrow{CH_2} C-\underset{\underset{\displaystyle C}{|}}{C}-C=C \xrightarrow{CH_2} C-\underset{\underset{\displaystyle C}{|}}{C}-C-C=C \xrightarrow{CH_2} C-\underset{\underset{\displaystyle C}{|}}{C}-C-C-C=C \xrightarrow{CH_2} C-\underset{\underset{\displaystyle C}{|}}{C}-C-C-C-C=C.$$

The contents of the C_5-, C_6-, C_7-, and C_8-fractions in the condensate were approximately 12,22,22 and 12% respectively.

The results of the fractionation were verified by the Raman-spectrum method. It was found that Fraction 6 consisted almost entirely of 2-methylpentane, which was estimated by reference to the following frequencies: 325 (9.5, 387 (2,b, double), 446 (15), 734 (3.8), 785 (2), 815 (28), 860 (2), 894 (5.7), 942 (3,b), 958 (9), 1015 (2), and others. Fraction 9 consisted practically entirely of 2-methylhexane, which was determined by reference to the following frequencies: 308 (13), 414 (3.5), 434 (4.5), 448 (1), 729 (2), 784 (5.4), 823 (11.2; sh), 874 (6.4), 894 (9.5, sh), 940 (3), 956 (6.3), 1062 (5.6, b), and others. Fraction 12 consisted mainly of 2-methylheptane, detected by the following frequencies: 288 (11.1), 409 (3.5), 763 (2.6), 816 (9.2), 879 (2.7), 895 (4.5), 952 (5.6; sh), 963 (5.6;sh), 1030 (2), 1044 (3) and others. Fraction 10 contained 2-methylhexane and 2-methylheptane, the former predominating; they were detected by the same frequencies as those cited above for Fractions 9 and 12.

SUMMARY

1. The reaction of catalytic hydrocondensation of carbon monoxide with straight-chain olefins has been extended to the simplest branched olefin, 2-methylpropene.



2. The average yield of liquid condensate was 550-650 ml/cu.m, or 62-69 ml/liter.hr, and the maximum yield attained 785 ml/cu.m, or 87 ml/liter.hr.

3. The liquid condensate contained 11% of unsaturated hydrocarbons and, after complete hydrogenation, 86.6% distilled over below 157°. The contents of C_5-, C_6-, C_7-, and C_8- fractions were 12,22,22 and 12% respectively. These fractions consist essentially of hydrocarbons having a methyl side group on the second carbon of the chain, i.e. 2-methylbutane, 2-methylpentane, 2-methylhexane, and 2-methylheptane respectively.

Received March 7, 1952

Institute of Organic
Chemistry of the
USSR Academy of
Sciences

LITERATURE CITED

[1] Ya. T. Eidus and K. V. Puzitsky, Proc.Acad. Sci. USSR 54,35 (1946).

[2] Ya. T. Eidus, N. D. Zelinsky, and K. V. Puzitsky, Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 1, 110 (1949).

[3] Ya. T. Eidus, N. D. Zelinsky, and K. V. Puzitsky, ibid, No. 3, 326 (1949).

[4] Ya. T. Eidus, N. D. Zelinsky, and N. I. Ershov, Proc.Acad. Sci. USSR, 60, 599 (1948).

[5] Ya. T. Eidus, N. D. Zelinsky, N. I. Ershov, and M. I. Batuev, Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 4, 377 (1950).

[6] N. D. Zelinsky, Ya. T. Eidus, K. V. Puzitsky, and M. I. Batuev, Ibid. No. 6, 647 (1950).

[7] Ya. T. Eidus, N. D. Zelinsky, K. V. Puzitsky, and N. I. Ershov, ibid, No. 1, 145 (1952).*

[8] Ya. T. Eidus, N. I. Ershov, M. I. Batuev, and N. D. Zelinsky, ibid, No. 6, 722 (1951).

---

* See Consultants Bureau translation, p. 157.

BLANK
PAGE

CHRONICLE

CONFERENCE ON THE TRANS-EFFECT PRINCIPLE

On 24-26th of March, 1952, a conference was held in Moscow on the trans-effect principle. It was organized by the N. S. Kurnakov Institute of General and Inorganic Chemistry of the USSR Academy of Sciences, and leading academic and industrial specialists on the chemistry of complex compounds, from Moscow, Leningrad, Kiev, Ivanov, Tbilisi, Kazan, Kishenev, Dnepropetrovsk, and other towns, took part in the proceedings. The problem put before the conference was that of finding methods of approach and experimental techniques that could lead to the establishment of the nature and quantitative characteristics of the trans-effect principle. The qualitative side of this principle and its importance in science and industry are now well understood: it is widely applied in the synthesis of new compounds and is of great significance for the further development of chemistry and modern technology; it is a concrete application of Butlerov's theory of chemical structure to the complex-compound field.

The discussion was opened by Academician M. M. Dubinin, secretary of the Division of Chemical Sciences of the USSR Academy of Sciences. "The present conference," he said, "being devoted to the discussion of one of the fundamental questions in the theory of the structure of inorganic complex compounds, is closely concerned with concepts based on a more general principle, discovered by Butlerov, and developed by Markovnikov and others. We may therefore regard the work before us as a further stage in the creative development by Soviet scientists of the theory of chemical structure. On the basis of numerous experimental investigations, commenced already during the lifetime of L. A. Chugaev, I. I. Chernyaev succeeded in establishing that mutual effects, precisely analogous to those found in organic chemistry, occur between atoms in the inner zone of complex compounds. The basic idea of the Chernyaev generalization, which is known as the trans-effect principle, is as follows: the strength of the bond between the central metal atom and any substituent is affected very little by the nature of adjacent atoms or groups of atoms, whereas atoms or molecules situated in a more remote region of the inner zone of the complex compound —that is to say, in the trans position—have a powerful effect on the chemical mobility and reactivity of this atom of the complex compound.

"During the 25 years that have elapsed since the discovery of the trans-effect principle it has received a sound experimental basis both in the investigations of Academician I. I. Chernyaev and his students, and also in those of other workers on the chemistry of the platinum metals. The range of the applicability of the principle has been greatly widened in recent years, and, as a result, Soviet chemists have been enabled to direct the course of chemical processes relating to complex compounds and to make a rational approach to the synthesis of compounds of previously determined composition and structure.

"Nevertheless, the physical nature of the trans effect still has no adequate theoretical basis. Investigations on the quantitative characteristics of the trans effect are still in the initial stages: their development is doubtless hindered by the greatly inadequate amount of material available on the application of the great variety of physical and physicochemical methods of investigating complex compounds. Another important direction of research comprises the development of L. A. Chugaev's views on the widening of the concept of the complex compound and the extension of this concept and its associated laws to derivatives of as many elements as possible. This path will lead to the removal of the chemistry of complex compounds from an isolated, circumscribed section of chemistry, essentially concerned with compounds of the so-called noble metals. Other important questions of principle are involved in the development of the theory of the structure of complex compounds: the causes underlying the trans effect may be similar to or identical with the causes underlying the mutual effects of atoms in the molecules of organic substances.

"Free discussion on all these questions, under the conditions for the development of true bolshevist criticism and selfcriticism, will enable us not only to appreciate the fundamental objective results of the theoretical and experimental investigations into the chemistry of complex compounds, but also to plan our further course of progress in conjunction with the development of our advancing materialistic theory of chemical structure".

The conference heard and discussed two papers: "The Experimental Basis of the Trans-effect Principle" by Academician I. I. Chernyaev, and "The Explanation of the Trans Effect" by Corr. Member A. A. Grinberg.

In Academician Chernyaev's paper on the experimental basis of the trans-effect principle the results of the lecturer and his school (A. D. Gelman, V. I. Goremykin, A. M. Rubinshtein, A. V. Adrianova, L. A. Nazarova, and others) were cited in confirmation of the fruitfulness and progressive role of the trans-effect principle, which is based on the further development of the materialistic structural theory of Butlerov and Markovnikov in its application to inorganic complex compounds. The trans-effect principle may be formulated as follows: in complex molecules having the form of a square or octahedron in the center of which the central metal atom is to be found, the reaction rate for the substitution of an addend (in the form of an atom or molecule) bound to the central atom is determined by the nature of the substituent-addend occupying the opposite end of the diagonal. Thus, the strength of the bond between the central atom and any substituent is affected to a very small extent by the nature of adjacent (cis) atoms or molecules, whereas atoms or molecules situated in the most remote part of the complex-compound molecule (trans) on the diagonal of the square or the axis of the octahedron greatly influence the chemical behavior of the complex molecule.

The value of the trans-effect principle as a scientific generalization lies also in the fact that it has not only explained the courses of reactions in the inner zone of complex compounds and not only unified and explained the previously discovered rules of Jorgensen, of Peyronel, and of Kurnakov, but has also brought them together to form a single, orderly whole and made it possible to predict the course of inner-zone reactions, even though the nature and quantitative side of this principle still remains unelucidated.

In Corr. Member Grinberg's paper a description was given of the attempts that have been made at various times by Soviet workers to explain the trans-effect principle; they are briefly as follows: Grinberg, and then Nekrasov, tried for the first time to make an approach to the elucidation of the nature and quantitative characteristics of the trans-effect principle starting from polarization concepts. Grinberg argued, that if in a complex compound having the form of a square three identical acid residues (addends) of identical polarizability are placed at corners and an acid residue (addend) differing from the other three and having a high polarizability is placed at the remaining corner, then, owing to the displacement of the center of gravity of negative charges in the direction of the substituent in the trans position to the fourth acid residue, the acid group at the opposite end of the diagonal to the fourth acid residue is weakened. Corr. Member B. V. Nekrasov in his solution of this problem started from the idea of a dipole induced in the central ion. When the acid residues (addends) are identical, an identical dipole is induced in each by the positive central complex-forming ion, leading to a strengthening, to an equal extent, in each of these bonds with the central ion. If one of the acid residues is replaced by another, different residue, a resultant dipole arises in the complex-former which depends on the nature of the newly introduced acid residue, and this is the greater in value, the greater the difference between its polarization properties and those of the other three groups. In other words, the deformability of the complex-former depends on whether the acid residue (addend) last introduced into the molecule of the complex compound has a greater or less polarizability. Thus, according to Grinberg and Nekrasov, the trans effect "is a special case of the phenomenon of contrapolarization".

The conference found that both of these treatments permitted limited, tentative, qualitative approaches to the elucidation of the nature and quantitative aspects of the trans-effect principle. The concepts developed by Grinberg and Nekrasov have now lost much of their value and may be regarded only in their historical perspective. It must be noted that these so-called polarization concepts are based on methodological errors, for they are based largely not on facts, not on direct experimental data, but on a great number of assumptions in calculations that do not really reflect any real phenomenon and cannot, therefore, characterize the nature and quantitative aspects of the trans effect. There have been also other attempts to elucidate the physical aspects of this principle, based on the establishment of the nature of the chemical bond between the central atom and a substitutent (Chernyaev and Gelman) and on the oxidation-reduction properties of inner-zone substituents (Grinberg). At the conference, also other ways of achieving this end were discussed; they were based on various principles, but they permitted the solution of the problems that had been set — the elucidation of the nature and quantitative characteristics of the trans-effect principle.

The papers of Academician Chernyaev and Corr. Member Grinberg contained certain errors of historical, scientific, and methodological character. In these papers there was to be found either none or very little reflection of the work of prominent Russian chemists such as Lomonosov, Mendeleev, Kurnakov, and Chugaev. In these papers no use was made of many of the investigations of Soviet scientists. In Corr. Member Grinberg's paper there was no clear formulation of the speaker's attitude to the so-called "theory" of resonance-mesomerism, which has so deleteriously affected progress in the chemistry of complex compounds. Hence, both of these speakers were justifiably criticized.

The papers gave rise to many questions and to a lively discussion, in which specialists in various branches of knowledge — chemists, physical chemists, and physicists — took part. The participants characterized in detail the prominent role and great significance of the trans-effect principle in the chemistry of complex compounds. Attention was drawn to the inadequate use that was being made of modern physicochemical and physical methods in the work directed to the elucidation of the trans-effect principle.

Professors Kedrov, Goremykin, and Gelman, in their speeches, discussed in detail the genealogical link connecting Chernyaev's trans-effect theory with the principles of Butlerov's materialistic theory of chemical structure, and they emphasized the great harm done by the anti-Butlerov, antiscientific, basicly idealistic concept of resonance-mesomerism, both in organic, and in inorganic chemistry.

Participants of the conference, particularly Professors Boky, Yakshin, Yatsimirsky, Babaev, and Ptitsyn, stated and considered the unanswered and disputed questions concerning the fundamental nature of the trans effect and the methods of solving this problem. They considered that polarization concepts based on electrostatics could not be of any help in the elucidation of the complex nature of the trans-effect principle. As is known, the attempts of Corr. Member Ya. K. Syrkin, on the basis of the erroneous concept of resonance-mesomerism, to replace the trans effect by cis-reinforcement did not in fact lead him to a positive solution of this problem, but had, on the contrary, a harmful effect and delayed for some time the normal development of this remarkable principle.

The participants of the conference unanimously condemned the so-called theory of resonance-mesomerism, which is fundamentally idealistic, as being pseudoscientific, and they brought forward a number of concrete proposals concerning the planning and coordination of scientific investigations in this branch of inorganic chemistry. Reference will now be made to the speeches of some of the participants of the conference on the trans-effect principle.

Prof. A. V. Babaeva paid a high tribute to the trans-effect principle, and she cited as an example of its value the fact that no platinum complex compound of the cis-diamine series containing hydroxylamine had been prepared in 70 years; now, guided by the trans-effect principle of Chernyaev, she had succeeded in bringing about this synthesis.

Prof. K. B. Yatsimirsky remarked that Grinberg in his paper had expressed pessimism in connection with the fact that no complete theory of the trans effect exists as yet. This is not altogether correct, the speaker pointed out. We must ask ourselves the question: What is a theory? If we answer that a theory is a generalization from experiment, then in this case we have a wide generalization from experiment, so that there is indeed already a theory. With regard to its interpretation, the matter is certainly not hopeless, as it might appear at a first glance. Yatsimirsky remarked that to limit the trans-effect principle only to kinetics would be harmful, because in fact we have to deal with two groups of complex compounds, which are different in principle: those which react in time, and those for which kinetics does not exist, i.e., those complex compounds that are broken down and formed instantaneously.

Prof. V. I. Goremykin said that, if we compare the results obtained by the Chugaev-Chernyaev school with the work done in this field abroad, it is easy to see that the work of the scientists of capitalist countries is distinguished by the absence of any such unifying idea; it may be characterized briefly as a jumble of ideas or as pure, undisguised empiricism. The leading role of the Chugaev-Chernyaev school of inorganic chemists, both in the USSR and elsewhere, can therefore be understood. Goremykin pointed out further the necessity of developing further the trans-effect principle, giving first consideration to the synthesis and investigation of the complex compounds of different metals, carrying out syntheses both in aqueous, and in nonaqueous solution, and studying the properties of complex compounds by modern physicochemical and physical methods. The speaker then pointed out the erroneous statement contained in the foreword to Chernyaev's and Grinberg's papers. It is there stated: "Investigation by the aid of X-radiograms can in principle replace the determination of molecular structure by chemical means". This statement is erroneous from the methodological point of view, for X-ray-structure analysis cannot replace all the variety and richness of chemical investigation.

Prof. G. B. Boky remarked that neither in the papers that had been given, nor in the introductory statement of the organizing committee were there any references, apart from some vague allusions, to the discussion "The

State of the Theory of Chemical Structure in Organic Chemistry". "It is well known," said Boky, "that the trans-effect principle was discovered and developed in the Soviet Union, and that practically no-one has denied the existence of the trans effect, the exceptions being a statement made long ago by Corr. Member I. A. Kazarnovsky in which he threw doubt on the priority of the discovery and its importance, and an unsuccessful attempt by Corr. Member Syrkin to show "theoretically" that the trans effect is only an apparent effect that is bound up with the concept of "cis-reinforcement". Neither of these assertions have received wide acceptance and have not had any essential effect on the development of work on the trans effect. Concerning the trans effect, we may now speak only of its being undervalued, of its being ignored, but not of its being criticized. The ways of the further development of the theory of the trans effect have not been indicated clearly in the papers; and yet the indication of these ways and the intelligent planning of research over a long period of time forms are the objectives of our conference, and these matters are always of prime importance and are often subjects that are ripe for discussion.

An important defect in both papers, in the speaker's opinion, was the complete disregard of the results obtained in recent years in crystal chemistry, developed on the basis of the immortal work of E. S. Fedorov. Another defect in Chernyaev's paper was undoubtedly the extreme narrowness of treatment. All the examples, without exception, were taken from the chemistry of platinum, whereas one of our primary problems is the extension of the trans-effect principle to other substances and to other fields in chemistry. Boky then discussed the way in which crystal-chemical and X-ray-structure methods enable us to approach the structure of complexes in its quantitative aspects; they enable us to measure the lengths of the coordinates of the complexes in centimeters, i.e., to measure the interatomic distances. The methods of classical chemistry do not offer such possibilities, and the ignoring of such material in Chernyaev's paper is therefore particularly to be regretted, for it is difficult to imagine that these methods are not known to him. A fundamental defect of Grinberg's paper is the exaggeration of the significance of electrostatic concepts, and again we find undervaluation of crystal-chemical data. Our most important immediate task, in the speaker's opinion, is the extension of investigations relating to the direct determination of magnitudes that characterize the effect quantitatively.

Ya. A. Fialkov, Corr. member of the Ukr.SSR Academy of Sciences, spoke of certain questions that had been discussed in connection with the problem of the trans-effect principle. The definition of the trans-effect principle formulated by the Organizing Committee merits, according to Fialkov, great attention in that it is based on the sum total of all the experimental results relating to the trans-effect principle. It does not go outside the limits of experiment, and, moreover, it defines a number of directions in which the further coordinated studies of this important theoretical generalization must proceed. It is impossible to agree completely with the formulation of the definition of the concept of the trans effect as given in the Organizing Committee's preamble, for it is not in conformity with Butlerov and Markovnikov's concept concerning the mutual effects of atoms bound together in a molecule.

B. M. Kedrov, Corr. member of the Academy of Pedagogic Sciences, remarked that the main problem of the conference was the thorough, detailed application of the fundamental ideas of the Butlerov theory to inorganic chemistry and, in particular, to one of its most important branches, the chemistry of complex compounds.

"Grinberg stated," Kedrov pointed out, "that he regarded Chernyaev's discovery not as a simple observation, as a simple group of unsystematic, ungeneralized facts, but as the discovery of a definite principle, or even law. This is quite true, but I would say that Grinberg abases the meaning of this law, putting it on the level of a fact and saying, in effect, these are concepts of the same order, whereas the concept of the trans effect is not only the discovery of a definite bond and relationship, but also an interesting interpretation; and again, not only interesting, but also as deeply and seriously applicable to the present phenomenon as an interpretation in organic chemistry, for here we have indeed an extension of the Butlerov principle to the field of inorganic chemistry".

It has been considered until now that Mendeleev made no pronouncement on the question of complex compounds, or, as he said, "molecular compounds"; there is very little about this matter in "The Principles of Chemistry". Apparently, Mendeleev did not concern himself with this question, either experimentally, or theoretically. Kedrov pointed out that in the second edition of Grinberg's "Chemistry of Complex Compounds" it is stated that Mendeleev did not carry out any experimental work with complex compounds." This is not true. In the Leningrad Museum there are about ten manuscripts and many laboratory notes relating to the study of complex compounds. This is particularly interesting, because the fundamental idea that lies at the basis of not only this problem, but also the whole of the chemistry of complex compounds, the idea of a central atom, owes its origin directly to Mendeleev.

"I consider that all this material is of great interest, particularly the article in which Mendeleev generalizes his views, criticizing the erroneous views of his contemporaries and attempting to develop correct ideas concerning platinum compounds, ideas that are extremely close to later concepts and are much closer to our ideas than were those of his contemporaries."

Prof. A. D. Gelman pointed out that Werner's coordination theory did not in anyway provide a scheme covering the behavior of chemical processes in the inner zone of complex compounds. This failing of the theory was remedied by Chernyaev's work, and if we make a comparison with organic chemistry, it must be said that Chernyaev has carried out the work that was done in the field of organic chemistry by Butlerov and Markovnikov. Gelman's investigations on unsaturated compounds — carbon monoxide, nitric oxide, and thioethers —, and also Grinberg's work on phosphines, have shown that these unsaturated molecules show a still higher trans effect than acid residues. It was at this point that the speaker proposed that the range of the trans-effect principle should be extended beyond that formulated by Chernyaev in 1926, i.e. that it should be considered that the place where reaction occurs in the inner zone of a complex compound is in the trans position to the active substituent, which may be not only an acid residue, but also a compound such as a thioether, nitric oxide, or carbon monoxide.

In Gelman's opinion, it is incorrect to try to explain the trans effect from a single point of view, as Grinberg and Nekrasov have tried to do — at first from the polarization point of view, and now from the point of view of reducing properties. We must make our approach while taking into account the properties of the substituents that can enter and form a complex molecule.

G. S. Zhdanov devoted his speech to the question of the trans effect in solid crystalline substances and to the prospects of crystal-chemical methods of investigating the trans effect. He pointed out the problem is extremely difficult and complex. In fact, exploratory investigations are essential. Sometimes it is impossible to come to a precise conclusion, particularly in gaseous media and in solutions. More reliable results can be obtained in the solid state, but, if we turn to crystals, we are faced with the necessity of making extremely exact measurements of interatomic distances. It is now clear that the trans effect has a value of the order of several angstroms. In this connection, the recently published work of Boky is of great interest: results of investigations on complex compounds are given, including bond lengths of ammonia - platinum — chlorine.

Prof. B. V. Ptitsyn remarked that the trans-effect principle discovered by Chernyaev has one excellent characteristic, which is common to all great generalizations, namely, that one gets use to it fairly quickly, and fairly soon the time comes when it appears strange how it was possible to manage previously without this principle. Chernyaev, in his paper, gave a detailed and full account of the experimental material that lies at the basis of the trans-effect principle, and he pointed out the facts that cannot be fitted into the principle.

The quantitative characteristics of the trans-effect principle may be arrived at from the change in valency in the process of complex formation, of which Chernyaev spoke in his paper when he pointed out that the trans effect cannot be characterized in terms of the usual valency; this was referred to also by M. M. Yakshin in his speech. Thus, by a comparison of potentials, it is possible to evaluate the degree of covalency of the bond and, ultimately, the value of the trans effect.

Prof. A. V. Ablov pointed out that the trans-effect principle discovered by Chernyaev for bivalent platinum compounds generalized the results of experiments on complex compounds and enabled us to predict the chemical behavior of these compounds and to map out the way to the synthesis of new compounds. This principle was extended by Chernyaev to cobalt compounds, and there also it was found to be true and to give fruitful results. The reduction of the trans-effect merely to a question of the definition of directed bonds, i.e. to the fact that bonds are directed, would not explain the difference in behavior between bi- and quadri-valent platinum on the one hand, and tervalent-cobalt on the other. It is of course necessary for the existence of the trans-effect that bonds should be definite, but only directed bonds are sufficiently characteristic for the appearance of the trans-effect.

Prof. L. M. Volshtein remarked that the trans-effect principle is a valuable guide to action in the work of chemists in the field of the complex compounds of bi- and quadri-valent platinum. As had been said, the trans-effect was exhibited by the other metals of the platinum group to a considerably smaller extent. For metals that do not belong to the platinum family the trans-effect is, practically speaking, absent or only barely apparent. It is obvious that these non-noble metals, as we may term them briefly, must take part in the mutual effects of atoms and groups of atoms. No one doubts this, but whether it is the trans-effect that is displayed, or the free action of addends situated in the trans-position, and to what extent it is displayed — these questions are difficult to answer in advance, while there are so few data concerning the trans effect for non-noble metals.

Others that joined in the discussion were Academician A. I. Frumkin, Prof. A. M. Rubinshtein, V. G. Tronev, A. V. Nikolaev, K. A. Semenchenko, and A. M. Klochko. There were twenty speakers in all.

When concluding statements had been made by Academician Chernyaev and Corr. member Grinberg, the conference carried a concrete resolution concerning the development of scientific research work on the chemistry of complex compounds.

Resolution of the Conference on the Trans-Effect Principle

Comrade J. V. Stalin, in his great work "Marxism and Questions of Linguistics", has clearly pointed the way that Soviet scientists must take for the further development of Soviet science in all branches of knowledge. Guided by Comrade J. V. Stalin's precept that "no science can develop or flourish without conflict of opinions, without freedom of criticism", Soviet scientists have recently held a number of creative discussions on various scientific questions.

The Conference on the Structure of Organic Compounds held in 1951 exposed the "Theory of Resonance or Mesomerism" as methodologically unsound, idealistic, and unfruitful, and it pointed out the way of further development in Soviet chemistry on the basis of the only correct scientific method of gaining knowledge — dialectical materialism.

Characteristics peculiar to our native chemistry are: the depth and wideness of our investigations, the linking of theory and practice, and the further development and utilization of our rich heritage from the great Russian chemists Lomonosov, Mendeleev, and Butlerov. Our native chemistry was always materialistic, and this tradition has received its further development in Soviet chemistry.

The last fifty years has seen the work in our country of such outstanding inorganic chemists as N.S. Kurnakov, who created a new chemical method (physicochemical analysis) and was a prominent investigator in the chemistry of complex compounds, and L. A. Chugaev, who founded the largest existing school of chemists working in the field of complex compounds.

There were attempts in recent years on the part of Ya. K. Syrkin and M. E. Dyatkina to drag the anti-scientific, ideologically unsound concept of resonance into inorganic chemistry also, and these attempts did not receive a timely and adequate check from inorganic chemists.

The trans-effect principle, as it developed, met with differing responses from foreign and from Soviet chemists. The foreign chemists either ignored it, or ascribed its discovery to foreign chemists. Certain Soviet chemists, for example I. A. Kazarnovsky and B. F. Ormont, have disparaged the role and importance of the trans-effect principle in the chemistry of complex compounds.

The Conference points out that Soviet chemistry occupies the first place in the world with respect to the synthesis, study, and application of complex compounds.

The trans-effect principle, which was discovered in 1926 by I. I. Chernyaev, is a further step forward along the road of progress in Soviet chemistry and is a creative act consequent on the fruitful scientific activity of the Russian chemists of the preceding epoch.

Chernyaev's principle is a concrete expression of A. M. Butlerov's theory of chemical structure in the field of complex compounds. This principle opens up the road to the synthesis of compounds having previously determined compositions, structures, and properties. The importance of the trans-effect principle in practice is exceptionally high: by its aid, numerous complex compounds of the platinum metals have been synthesized, new analytical methods have been developed, and technical processes for the preparation of platinum metals from new raw materials have been worked out.

The Conference notes that work on the elucidation of the nature of the trans-effect has been carried out by I. I. Chernyaev, A. A. Grinberg, B. V. Nekrasov, and A. D. Gelman, all of whom have played a positive part in the clarification of certain aspects of the trans-effect. At the same time, the Conference finds that the work done on quantitative aspects of the trans-effect is still inadequate.

The Conference considers that it is essential to intensify work in this direction in order to obtain the data necessary for the creation of a general theory of the trans-effect.

Studies of the trans-effect have been confined hitherto mainly to complex compounds of the platinum metals. However, investigations into the mutual effects of coordinated groups in complex compounds of other elements are being carried out in various cities in our country (Kiev, Leningrad, Ivanovo, Tbilisi, Kishenev, Dnepropetrovsk, etc.), but they are still inadequate.

The further development of these investigations is hindered by the absence of adequate coordination of scientific investigations in this field.

The most important problems in the development of the theory of the structure of complex compounds on the basis of the trans-effect principle and of the achievements of modern science are the following:

1. Determination of the quantitative characteristics of the trans-effect by various methods, namely:

a) classical chemical methods, with consideration of the effect of the medium;
b) crystal-chemical methods;
c) physicochemical and physical methods: labeled atoms, thermochemical and thermographical, electrochemical (conductivity, potential changes, polarography, ion transfer, etc.), electrical (dipole moment and dielectric constant determinations), X-ray-structure analysis, magnetometry, etc.

2. Further development of work on the synthesis of complex compounds of various elements, on the physicochemical study of their chemical structures, on their reactivities, and on their application.

3. In order to coordinate and plan scientific investigations in the field of complex compounds, the Conference considers that it is essential to set up a committee of the Council of the N. S. Kurnakov Institute of General and Inorganic Chemistry of the USSR Academy of Sciences. In particular, this committee will be given the task of composing a plan for research work in 1953.

4. In order to develop the study of the trans-effect from all sides, it is essential to bring in workers representing allied branches of science.

5. The USSR Academy of Sciences is asked to publish the transactions of this conference in the Bulletin of the Platinum Sector. They are asked also to speed up the publishing of selected works of L. A. Chugaev.

6. It is considered essential that selected works of Russian workers on the chemistry of complex compounds should be published.

7. It is considered essential that the Sixth All-Union Conference on the Chemistry of Complex Compounds should be called for January 1953.

The Conference calls upon all workers on the chemistry of complex compounds to develop further the use of criticism and self-criticism in scientific work, to unmask any attempts to intrude hostile ideology into science, to strengthen the link of theory with practice, and to make every effort to complete the historic task set by Comrade Stalin: ". . . . not only to equal, but to surpass in the near future the achievements of science in foreign countries"*.

Session in Honor of the Bicentenary of the Foundation of the Science of Physical Chemistry by M. V. Lomonosov

On May 28th, 1952 there was held a joint session of the Division of Chemical Sciences, the L. Ya. Karpov Physicochemical Research Institute of the Order of the Red Banner of Labor, and the Chemistry Faculty of the M. V. Lomonosov Moscow State University of the Order of Lenin, and papers were read in honor of the bicentenary of the foundation of the science of physical chemistry by M. V. Lomonosov: "M. V. Lomonosov, Founder of Physical Chemistry" by Prof. S. V. Kaftanov, "The Work of M. V. Lomonosov on Atomistics, and its Significance for the Development of Chemistry" by Prof. N. A. Figurovsky, and "M. V. Lomonosov's Investigations on Solutions" by Prof. S. V. Gorbachev.

Academician M. M. Dubinin, opening the session, spoke of the services that M. V. Lomonosov had rendered and of his great love of his own people, to whom he devoted his strength and that which was most dear to him — his science.

S. V. Kaftanov emphasized in his paper that among the famous men that had risen in the great Russian nation and had contributed immense riches to the treasure house of world culture, M. V. Lomonosov occupies a special place: his dissertation "The Action of Chemical Solvents in General" (1743) constituted the first work in physical chemistry. Of this paper Lomonosov himself wrote: "This theory of solutions based on chemical experiments and physical principles is the first example and pattern for the foundation of true physical chemistry. . .". Throughout his scientific career, Lomonosov was an advocate for the wide application of physics, chemistry, and mathematics in investigations. These sciences are found applied in combination in his crowning work: "Introduction to True Physical Chemistry" (1752).

In his paper N. A. Figurovsky referred to the definition of physical chemistry given 200 years ago by M. V. Lomonosov: "Physical chemistry is the science that explains on the basis of physical laws and experiments that which occurs in mixed chemical bodies subjected to chemical operations. It may be called chemical philosophy, but in a completely different sense from the mystical philosophy in which not only are no explanations given, but even the operations themselves are carried out in a mysterious manner. We decided to call this work physical chemistry because we had determined to include in it only that which would lead to a scientific explanation of the mixing of bodies. We therefore consider it essential to exclude everything relating to economic sciences, to pharmacy, to metallurgy, to glass technology, etc. and to place these subjects in a special course of technical chemistry." The speaker said also that physical chemistry has now penetrated into the whole of modern science and technology and that there was no need to enlarge on its importance and significance. "The history of chemistry cannot take the view that outstanding scientific discoveries, new generalizations, and the beginnings of new important trends in the evolution of chemistry are chance events," continued Figurovsky. "It is obvious that, in the external circumstances of Lomonosov's work and in the scientific activity itself of that great scientist, there existed deep roots, which at a definite moment gave out powerful shoots of the new scientific discipline of physical chemistry". The speaker made an analysis of the reasons for the remarkable discoveries of M. V. Lomonosov. The breaking up of feudal society, the growth and spreading of commercial capital, and the rise of capitalist industry in the West and of native manufacturing concerns based on serfdom in Russia (owned by the Demidovs, Stroganovs, and others) all had their effects on the grave upheavals that occurred in the productive efforts of society. Reorganization of the social-economic structure of society occurred, and in the middle of the eighteenth century a new epoch began in the evolution of science and technology — an epoch of great technological changes, inventions, and scientific discoveries. The whole scientific activity of Lomonosov reflected the upheavals that were occurring in the economy of the country. Lomonosov was an innovator in science and an enemy of traditional routine: his work was based on the rejection of old, traditional, misleading ways in science and on the search for new ways of progress. He boldly blazed new trails in all that he undertook — here lies the reason for his remarkable discoveries, here lies the greatness of his scientific creativity.

The development of Lomonosov's capacity for critical thought was influenced greatly by his broadly based education and by the training that he had received in mathematics, physics, and chemistry, which was no doubt facilitated by the process of emancipation from set traditions that was going on in science at that time.

The majority of workers in chemistry who were forerunners or contemporaries of Lomonosov were medical men by education and profession and were enslaved by traditional pharmacy, regarding chemistry as the art of preparing medicines, and not as a science. Lomonosov examined the contents of chemistry from the point of view of a scientific investigator and materialist who had rejected the traditions and prejudices of his time. The starting point and basis of his "Course of True Physical Chemistry" was his system of corpuscular philosophy, which he had worked out in its basic details and which formed the basis of his scientific work. Another starting point in the writing of the "Course of True Physical Chemistry" was to be found in the teaching activities of Lomonosov, who had an ardent desire to pass on the knowledge he had acquired to the youth of Russia.

Figurovsky showed in his paper that, whereas those not acquainted with the history of chemistry had asserted that Lomonosov gave us only the name "physical chemistry", he, in fact, created in the middle of the seventeenth century a complete scientific system on the basis of atomistics that was quite new at that time. By the aid of atomistics, Lomonosov developed ideas about chemical processes, explained many phenomena, and created a number of theories.

Prof. S. V. Gorbachev showed in his paper "M. V. Lomonosov's Investigations on Solutions" the way in which M. V. Lomonosov correctly estimated the significance of the theory of solutions in physical chemistry. Lomonosov was the first to distinguish dissolution processes from reactions such as the "dissolution" of zinc in sulfuric acid, and he formed the conviction that the heat change in the process could serve in practice as a criterion for the distinguishing of reactions and solution processes. Lomonosov's ideas on the nature of the heats of solution and of chemical reaction were expounded by him theoretically in such a convincing fashion that they retained their significance and recognition for a century and a half. Berzelius in 1842 repeated Lomonosov's views almost in full. The speaker described the transition from Lomonosov's principle to the new, more profound principle of Mendeleev, which, while not rejecting the effect of the mutual attraction of particles with chemical combination and evolution of heat, supplemented these ideas by consideration of accompanying physical processes that have their own thermal effects. The theoretical views of M. V. Lomonosov turned out to be extremely fruitful: on its basis and on the paths of its further development were founded the theory of the passage of electricity through solutions, the concept of osmotic pressure, the theory of electrolytic dissociation, and the theory of strong electrolytes.

BLANK
PAGE

TOWARD NEW SUCCESSES OF SOVIET CHEMISTRY

The publication of that work of genius by Comrade Stalin "Economic Problems of Socialism in the USSR", and the recent XIX Congress of the Communist Party of the Soviet Union have been great events in the life of our country. The resolutions and the agenda of the XIX Party Congress, and Comrade Stalin's speech, which was a fighting program of action, of great historical and international importance, inspire the Party and the whole Soviet nation to engage in the most self-denying struggle for new triumphs in the building of communism.

Comrade Stalin's work "Economic Problems of Socialism in the USSR" is devoted to the discussion of the most basic problems of the political economy of socialism. In it, Comrade Stalin presents in plain and convincing language the economic laws of socialism, and determines the basic conditions for the gradual transition from socialism to communism. The discovery by Stalin of the basic economic laws of socialism is of the utmost importance. "The most vital features and requirements of the basic economic law of socialism", declares Comrade Stalin, "might be formulated more or less in the following way: the assuring of the maximum satisfaction of the constantly growing material and cultural demands of the whole community by means of the continuous growth and improvement of socialist production based on higher technology".* This definition reveals the very essence of socialism. In order to achieve the actual transition from socialism to communism Stalin pointed to the necessity of achieving three basic preliminary conditions. First the continuous growth of social production must be assured, with particular stress on the production of means of production. Second it is necessary, by gradual steps, achieved at a rate acceptable to the kolkhozes, and hence to the community as a whole, to elevate kolkhoz property to the level of national property generally, and to convert commerce into a barter system. Finally, a cultural level of the community must be achieved such that all of its members are assured of the possibility of full development of their physical and intellectual capabilities.

The realization of the conditions pointed out by Stalin in his work is the task of the entire Soviet nation, which is triumphantly building communism under the leadership of the Communist Party, under its great leader and teacher Comrade Stalin.

Among the resolutions of the XIX Party Congress was the following: "The chief tasks of the Communist Party of the Soviet Union now are to build up a communist society by gradual transition from socialism to communism; continuously to raise the material and cultural level of the community; to bring up the members of the community in a spirit of internationalism and brotherly relations with the workers of all countries; and in every way to strengthen the active defence of the Soviet Fatherland against the aggressive acts of its enemies".**

There can be no greater privilege for Soviet scientists than to take the most active part in this great undertaking. The chief duty of Soviet chemists is to contribute to the continuous growth of communal production, and to the raising of the general cultural level of the community.

The directives of the XIX Congress relating to the Five-Year Plan for the development of the USSR contain the basic points of Stalin's work on economic problems. The Five-Year Plan for 1951-1955 is a great new step forward on the path of our progress toward communism.

Great and responsible tasks confront Soviet chemists who are engaged in the fulfilment of these directives. It will suffice to point out that the growth in the production of some of the most important chemicals is of the following order: caustic soda 79%, soda 84%, mineral fertilizers 88%, synthetic rubber 82%, cement 120%. A large increase in production of non-ferrous metals is envisaged, as follows: refined copper by 90%, lead 2.7 - times, aluminum not less than 2.6 times, zinc 2.5 times, nickel by 53%, and tin by 80%.

---

* I. Stalin. Economic Problems of Socialism in the USSR. State Political Press, 1952, p. 40.

** "Statute of the Communist Party of the Soviet Union". "Pravda" 1952, 1.

In connection with the projected increase in power supply during the current Five-Year Plan, resulting from the completion of such hydroelectric stations as that of Kuibyshev, Gorki, and Ust-Kamenogorsk, and in particular from the commencement of work on the exploitation of the power resources of the Angara River, the question of the use of local sources of raw materials for the aluminum, chemical, and other industries will arise.

The Five-Year Plan envisages considerable increase in the capacity of primary oil refineries, and of the fuel gas industry. The wider use of gas is intended, both for domestic purposes and as an automobile fuel, and as a source of chemical raw materials. The directives mention the importance of plant production for the needs of chemical industry.

Chemical industry is charged with the rapid and considerable increase of the mineral fertilizers, the soda, and the synthetic rubber industries. Special stress is laid on the general development of the synthetic rubber industry based on the use of gaseous petroleum products.

Apart from basic chemicals, the Plan envisages increase in the production of plastics, dyestuffs , raw materials for the rayon industry, and a widening of the assortment of other chemicals. Considerable tasks also confront the paper, the wood chemical, and the hydrolytic industries.

The continuous growth in socialist production, and the raising of the productivity of the work of the community, should raise the national income of the USSR during the five years by not less than 60%.

The directives impose special tasks on Soviet scientific institutions: "To improve the work of the scientific research institutes and of the higher educational establishments, and to make fuller use of scientific resources for the solution of the more important problems of development of the national economy, for the generalization of research results, and for the wider practical application of scientific discovery. In every way to collaborate with scientists in the development of their theoretical problems in all domains of knowledge, so as to strengthen the bonds between science and industry". *

G. M. Malenkov, in reading the report of the Central Committee to the Congress, showed that in the struggle for further technical progress our science has to play an important part, in that by its discoveries it helps the Soviet nation to discover and exploit more fully our national resources. The Party has imposed a definite task on Soviet science: "To develop further progressive Soviet science, which should occupy the leading place in world science. To direct the efforts of scientists toward the more rapid solution of the problems of the utilization of the enormous natural resources of our country. To strengthen the creative collaboration of science and industry, bearing in mind that this collaboration strengthens the experimental basis of science, and at the same time helps the industrial workers to solve their problems more quickly". **

The chemical institutes of the Academy of Sciences, USSR, are developing their work in accordance with the fifth Five-Year Plan. The great majority of the workers of these institutes takes part in solving the more important problems of development of the national economy. It is essential that the work of scientific research institutes should be properly coordinated, both in the Academies of Science and in the educational establishments of the Soviet Union. The concentration of scientific resources on the study of key problems is an essential condition for their better solution.

Parallel with the elucidation of theoretical problems of chemistry, the Institutes of the Division of Chemical Sciences should display more initiative and confidence in the application of the discoveries made by them to national economy. Of the theoretical problems which should above all engage the attention of chemical institutes, that of the theory of chemical structure is one of the most important. Not less important are the theoretical elucidation of the problems of velocity of chemical processes, of the reactivity of compounds, and of the thermodynamics of chemical reactions, and the study of the connection between the physical properties and the chemical structure of natural and synthetic high molecular substances. Much more attention should be given to the study of protein chemistry and of that of biogenic substances.

Modern chemical and physical methods of study should be more and more widely applied to scientific research; this refers particularly to the use of radioactive and stable isotopes as labelled atoms.

---

* Directives of the XIX Party Congress on the Five-Year Plan for the development of the USSR, for 1951-1955. State Political Press, 1952, p. 28.

** G. Malenkov. Report to the XIX Party Congress on the work of the Central Committee VKP (b). State Political Press, 1952, p. 78.

Soviet chemists are confronted with the task of collaborating with other scientists in order, by a profound investigation of theoretical problems, to achieve generalizations of a fundamental character. One of the stages of this work should be the publication of monographs on the more important divisions of chemistry.

The Soviet Government and the Party have devoted much attention to the work of scientists. In no country do there exist such favorable conditions for the development of science as have been provided in our country. Suffice it to say that the number of scientific research institutes, laboratories, and other scientific institutions in the USSR has risen, as was reported by G. M. Malenkov at the XIX Party Congress, from 1560 in 1939 to 2900 at the beginning of 1952, and the number of scientific workers has doubled over the same period. During the last Five-Year Plan period the State has spent 47.2 milliard roubles on the development of science.

G. M. Malenkov reported that, as a result of the efforts of the Central Committee of the Party, many domains of science were found to be fostering outlooks and traditions which were alien to Soviet people, and to tolerate the establishment of closed castes of scientists, and to be intolerant of criticism. Various manifestations of bourgeois ideology were revealed and eradicated, as were also all sorts of vulgarizing deviations. "Discussions in the domains of philosophy, biology, physiology, linguistics, and political economy have revealed serious ideological shortcomings in various domains of science, and gave an impulse toward the levelling of criticisms and the conflict of views, and have thus contributed to the development of science. Arakcheyev regimes existing on many sectors of the scientific front have been overthrown. There still persist, however, in a number of branches of science, incompletely liquidated monopolist cliques, which avoid contact with the younger generation of scientists and who fence themselves off from criticism, attempting to settle scientific problems by administrative means. There can be no branch of science which can develop successfully in the stuffy atmosphere of mutual admiration and overlooking of each other's errors; attempts at creation of such cliques of scientists lead inevitably to stagnation and decadence in science".*

A number of Soviet scientists have also fallen into grave error regarding the theory of chemical structure. The 1951 discussions of the state of this theory in organic chemistry disclosed certain ideological errors, and indicated the way toward the further fruitful development of A. M. Butlerov's materialistic theory. It is essential that we should continue to strive for such a state of affairs of science in which all the more important problems of theory, in all of the branches of chemistry, are developed according to the progressive ideas based on dialectical materialism.

Soviet chemistry has based its development on the glorious traditions of Lomonosov, Mendeleev, Butlerov, and other Russian scientists. The very numerous cadres of highly qualified Soviet chemists have, by their creative work, shown that they are capable of performing the greatest tasks which our Fatherland and the Party may entrust to Soviet chemical science.

Inspired by the resolutions of the XIX Congress of the Communist Party, our chemists will march confidently with the nation towards the triumph of communism, under the leadership of our leader and teacher, the architect of communism, beloved Comrade Stalin.

---

* G. Malenkov, loc. cit., p 95.

BLANK
PAGE

ADSORPTION OF GASEOUS MIXTURES

PART 2. ADSORPTION OF ETHYLENE AND PROPYLENE ON ACTIVE CHARCOAL

B. P. Bering and V. V. Serpinsky

1. Introduction

It was shown in Part 1 of this series [1] how important is the systematic study of simultaneous adsorption of mixtures of gases on adsorbents of different structure and nature. These studies are important, first because they contribute to the widening and deepening of current theoretical views on adsorptional phenomena generally, and second because they are necessary (although not always adequate) for the understanding, and the quantitative treatment, of the more important practical applications of adsorptional phenomena, in particular, the use of adsorbents for the separation of mixtures. The present paper is devoted to the study of simultaneous adsorption of ethylene and propylene on activated charcoal.

2. Experimental

The same methods and apparatus were used in this study as in that of simultaneous adsorption of ethylene and carbon dioxide [1]. The method depends on mixing known volumes of each of the gases, followed by measurement of the total pressure and the composition of the equilibrium mixture, determined by means of a precision gas analyzer, the action of which is based on the dependence of the thermal conductivity of a gaseous mixture on its composition and pressure.

We shall here describe only certain slight modifications which we have introduced into the apparatus described in Part 1 of this series [1]. Our basic concern was to stabilize the working of the gas analyzer and this was achieved by reducing to ~90° the temperature of the electrically heated wire of the analyzer, which was made of platinum, "extra" quality, diameter 30 μ. According to the new values of "cold" resistance of the wire and of the new "working" temperature chosen for this wire we varied the constant resistances forming the other three branches of the Wheatstone bridge. In its present form, the gas analyzer possesses not only the required high sensitivity (for $C_2H_4 + C_3H_6$ the analyzer is sensitive to changes in the content of either constituent of the order of 0.05%), but also shows high stability of calibration curves with time.

The next modification introduced into the apparatus consisted of immersing the general air thermostat containing the bulb with the adsorbent with the tubes leading into it in a second thermostat through which water from an ultra-thermostat was allowed to flow. This arrangement permitted us to make measurements of adsorption at different temperatures. Special tests were made to ensure that the gas coming into contact with the adsorbent had enough time to assume the temperature of the water thermostat, at the given rate of circulation of the gas, determined by the design and dimensions of the glass circulatory pump.

Measures were taken to reduce to a minimum any pockets of gas which could escape the general circulation, thus somewhat shortening the time needed for achievement of adsorptional equilibrium.

The same granulated activated charcoal was used as in the previous experiments, and ethylene was prepared and purified by the methods described in detail in Communication 1 [1]. The effectiveness of these methods, and the uniformity of the charcoal used, are very well illustrated by the practical identity of the adsorption isotherms with those presented in Communication 1.

Propylene was prepared by a slightly modified Senderens method [2], by dehydration of isopropanol in presence of fused anhydrous sodium bisulfate, at 120-140°. iso-Propanol was added gradually to the $NaHSO_4$ in a round-bottomed flask fitted with a reflux condenser, immersed in an oil bath, and the gas was collected in a gasometer, after passing it through wash-bottles containing 10% and 50% aqueous KOH. The gas was passed through a bulb immersed in liquid nitrogen, in order to freeze out the propylene, which was then distilled back into the gas-holder; we collected only the fraction boiling within a range of 1-2°, rejecting the initial and final portions of distillate. This operation was repeated several times, and the final product was passed over fused calcium chloride and phosphorus pentoxide, and collected in a bulb immersed in liquid nitrogen, sealed to the adsorption chamber. After exhaustive evacuation of the reaction space, the propylene was transferred to a storage vessel, passing on the way through a column of previously ignited and degassed active charcoal with silica gel. This last operation was described in detail in Communication 1 of this series.

3. Experimental Results

The methods described were applied to measurement of adsorption of the separate components: ethylene at 7° and 25°, at 0-760 mm, and propylene at 7 and 25°, at 0-300 mm. Adsorption of mixtures of the gases was studied at the same temperatures, over the range of pressures 0-300 mm, for the whole range of compositions of the equilibrium mixtures.

Since there are practically no data to be found in the literature for mixtures of gases, and since such data are necessary for the checking of theoretical concepts relating to adsorption of mixtures, we think it would be useful to present our experimental results in tabular form.

In Tables 1-4, as also in succeeding ones, the subscript "1" relates to the less strongly adsorbed gas, ethylene, and the subscript "2" to the more strongly adsorbed propylene. The pressures p are given in mm, and the magnitude of adsorption a in mM/g.

In studying adsorption of mixtures every series of measurements began with introduction of a known volume of propylene into the system, and after determining the equilibria a and p, successive portions of ethylene were added, keeping the amount of propylene constant. In Tables 3 and 4 each series of measurements begins with a partial pressure of ethylene $p_1 = 0$.

TABLE 1

Adsorption of ethylene at 7° and 25°

p_1	a_1	p_1	a_1
t = 7°			
4.5	0.214	90.6	1.089
10.2	0.349	115.9	1.218
19.7	0.505	147.6	1.359
28.4	0.615	183.7	1.500
38.7	0.721	237.0	1.667
48.8	0.805	290.3	1.813
61.0	0.898	338.3	1.928
68.8	0.957		
t = 25°			
4.1	0.093	137.6	0.938
6.2	0.137	161.5	1.017
9.4	0.193	204.6	1.138
12.6	0.228	220.5	1.179
16.1	0.278	268.3	1.292
22.1	0.345	330.2	1.420
36.0	0.460	381.2	1.501
48.0	0.545	494.0	1.686
64.0	0.631	579.4	1.804
75.6	0.687	679.5	1.928
91.0	0.767	771.3	2.030
104.2	0.810		

TABLE 2

Adsorption of propylene at 7° and 25°

p_2	a_2	p_2	a_2
t = 7°			
0.2	0.161	80.0	2.422
1.8	0.619	95.0	2.525
7.6	1.149	104.0	2.573
17.5	1.542	138.0	2.732
18.7	1.590	173.7	2.863
25.4	1.751	214.8	2.987
33.9	1.915	220.7	3.005
34.7	1.927	254.5	3.086
46.4	2.092	292.2	3.164
58.0	2.234	333.8	3.240
t = 25°			
3.3	0.570	104.1	2.081
7.6	0.802	121.5	2.175
8.3	0.828	139.9	2.260
15.8	1.081	188.6	2.439
25.3	1.296	192.0	2.435
38.0	1.504	237.0	2.585
39.8	1.521	252.5	2.611
54.4	1.703	256.5	2.621
73.5	1.878	280.2	2.679
77.3	1.904	325.5	2.760

4. Discussion of Results

In its general outlines the adsorption of ethylene-propylene mixtures on activated charcoal closely resembles that for ethylene-carbon dioxide mixtures [1]. In representing the experimental results for adsorption of mixtures we plot the equilibrium partial pressures of both gases, p_1 and p_2, on two axes, and on the third coordinate axis we plot the values a_1 and a_2 for the adsorption of each component, and also the value for summated adsorption $a_{12} = a_1 + a_2$.

For both the temperatures studied (7° and 25°), the adsorption surfaces for ethylene, $a_1 = f_1(p_1, p_2)$, and propylene, $a_2 = f_2(p_1, p_2)$, as well as that for summated adsorption, $a_{12} = f_3(p_1, p_2)$, which we do not represent in this paper in order to save space, have practically the same appearance as do the corresponding surfaces for the system CO_2–C_2H_4. Certain differences are apparently due to the closer resemblance of the C_2H_4 molecule to C_3H_6 than to CO_2, and to the greater difference between adsorption of ethylene and propylene than between ethylene and carbon dioxide.

TABLE 3

Simultaneous adsorption of ethylene and propylene at 7°

p_1	p_2	a_1	a_2	p_1	p_2	a_1	a_2
0	17.5	0	1.542	88.0	69.9	0.201	2.223
10.9	17.8	0.052	1.542	123.8	75.2	0.271	2.218
30.4	19.3	0.137	1.541	184.7	83.8	0.373	2.209
82.2	22.9	0.315	1.540	229.3	90.1	0.441	2.203
114.3	25.9	0.426	1.534	0	95.0	0	2.525
176.2	29.1	0.579	1.531	28.5	100.4	0.052	2.520
270.3	36.2	0.777	1.525	67.2	108.8	0.122	2.512
0	33.9	0	1.915	116.6	116.6	0.194	2.504
11.1	35.6	0.040	1.913	173.5	128.3	0.278	2.493
32.1	37.6	0.108	1.911	0	138.0	0	2.732
58.5	40.7	0.185	1.908	29.1	142.2	0.042	2.728
102.8	45.3	0.295	1.904	57.5	150.2	0.090	2.720
151.3	49.6	0.400	1.900	95.5	156.5	0.137	2.714
203.8	56.2	0.506	1.894	157.7	168.7	0.216	2.703
250.3	60.2	0.584	1.890	0	220.7	0	3.005
0	58.0	0	2.234	20.3	224.5	0.024	2.994
14.1	59.4	0.038	2.233	75.2	235.6	0.085	2.983
27.3	61.7	0.072	2.230				

The results obtained for the system C_2H_4–C_3H_6 are in full agreement with the more important qualitative conclusions made on the basis of an analysis of the behavior of the system C_2H_4–CO_2.

Fig. 1 represents sections of the adsorption surface for propylene, $a_2 = f_2(p_1, p_2)$, at 25°, by the planes p_1 = const., at the partial pressures of ethylene 0, 50, 100, 200, and 250 mm. It is evident that considerable variations in ethylene concentration have little effect on adsorption of propylene, and do not change the shape of the adsorption isotherms. The effect on adsorption of ethylene of varying propylene concentration is quite differerent, however, as appears from Fig. 2, which represents sections of the adsorption surface for ethylene $a_1 = f_1(p_1, p_2)$ by the planes p_2 = const., corresponding with the partial pressures of propylene 0, 5, 12.5, 25, 50, 100, 150, and 200 mm. Even quite small concentrations of propylene in the gaseous phase greatly depress adsorption of ethylene, and change the shape of the isotherms of this component. With values of p_2 as low as 5 mm the adsorption isotherm for ethylene becomes far less convex, while with a partial pressure of 50 mm of propylene the isotherm becomes nearly a straight line, i.e., a broadening of the Henry region occurs. The corresponding sections for 7° are of the same nature. We first encountered this straightening effect on the adsorption isotherms of the less strongly adsorbed component when studying the system CO_2–C_2H_4, when we explained it as being due to the heterogeneity of the surface of the charcoal. As will be shown below, this explanation receives further confirmation when considered from the point of view of heats of adsorption of gaseous mixtures.

TABLE 4

Simultaneous adsorption of ethylene and propylene at 25°

p_1	p_2	a_1	a_2	p_1	p_2	a_1	a_2
0	7.6	0	0.802	46.9	82.2	0.094	1.870
17.8	8.2	0.092	0.801	87.1	86.0	0.159	1.866
52.0	10.0	0.236	0.800	148.0	93.9	0.254	1.859
115.3	13.7	0.452	0.796	213.6	101.5	0.343	1.852
207.9	17.3	0.686	0.793	0	121.5	0	2.175
269.0	20.2	0.814	0.790	20.1	124.2	0.032	2.172
0	39.8	0	1.521	39.2	127.5	0.061	2.169
17.1	40.8	0.046	1.520	120.3	142.4	0.172	2.155
47.7	43.7	0.121	1.518	169.0	148.6	0.229	2.149
126.3	49.9	0.275	1.516	0	192.0	0	2.435
173.7	54.8	0.371	1.507	35.3	200.0	0.046	2.427
259.0	61.1	0.503	1.502	88.1	210.5	0.106	2.417
0	73.5	0	1.878	0	256.5	0	2.621
17.0	77.2	0.035	1.874	35.7	266.8	0.036	2.612

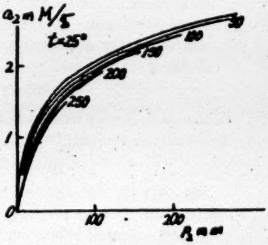


Fig. 1. Sections of the surface $a_2 = f_2(p_1, p_2)$ by the planes p_1 = const.

In our previous paper we introduced, for the characterization of selectivity of adsorption of the more strongly adsorbed component, the so-called selectivity coefficient α_2, determined by the equation

$$\alpha_2 = \frac{N_2^{\sigma} N_1}{N_1^{\sigma} N_2} = \frac{N_2^{\sigma}}{N_1^{\sigma}} \frac{p_1}{p_2} = \frac{a_2}{a_1} \frac{p_1}{p_2} . \qquad (1)$$

where N_2^{σ}, N_1^{σ} and N_2, N_1 are the molar proportions of each component in the adsorbed and the gaseous phase, respectively, and p_2 and p_1 are the partial pressures of the components in the gaseous phase. For the system CO_2–C_2H_4 the coefficient α_2 for ethylene remains approximately constant at constant total pressure, but diminishes with increase in total pressure. For the system C_2H_4–C_3H_6 the selectivity coefficient for propylene is not constant at constant total pressure, and falls slightly with increasing N_2 of propylene in the gaseous phase, and with rising total pressure.

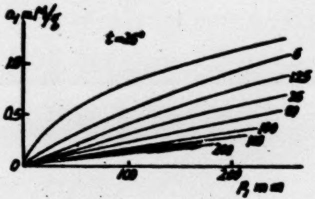


Fig. 2. Sections of the surface $a_1 = f_1(p_1,p_2)$ by the planes p_2 = const.

Fig. 3 shows the relation between N_2^{σ} and N_2 of propylene, at a total pressure of 300 mm, at 7° and 25°. It appears from these curves that the coefficient α rises slightly with falling temperature. Thus the value of the selectivity coefficient varies inversely with total pressure and temperature.

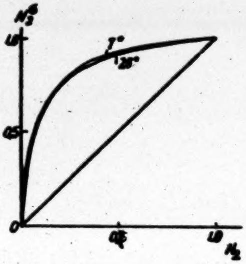


Fig. 3. Relation between molar proportion of propylene in the adsorbed phase N_2^{σ} and its molar proportion in the gaseous phase N_2 at 7° and 25°.

For the system C_2H_4–C_3H_6 the coefficient α remains approximately constant for the vertical sections of the adsorption surfaces made along the lines of constant summated adsorption, a_{12} = const., which we shall call sections of constant total filling of the surface; constancy of α is not observed in the sections of the adsorption surfaces by the planes of constant total pressure P = const. For the system CO_2–C_2H_4 the coefficient α remains practically constant for both the sections P = const. and a_{12} = const., probably because it does not greatly depend on pressure, and the given sections do not differ as much from each other as do the corresponding ones for the system C_2H_4–C_3H_6.

Fig. 4 represents projections of adsorption isosteres of both components a_1 = const. and a_2 = const. on the coordinate surface $a_1 = 0$ at 25°. The family of adsorption isosteres for propylene a_2 = const. approximates fairly close, a family of straight lines. The figures placed near the ends of these lines on the p_2 axis represent adsorption of propylene in mM/g. The family of adsorption isosteres for ethylene is a system of curved lines, the curvature of which gradually diminishes with increase in p_1. The figures placed at the points of intersection of these curves with the line representing constant total pressure P = 300 mm represent adsorption of ethylene in mM/g. A closely similar system of isosteres was obtained at a different temperature (7°).

The isosteres of Fig. 4 served for the construction of the isosteres of total adsorption $a_{12} = a_1 + a_2$, which are represented in Fig. 5, in which the 25° isosteres are shown as broken lines, and the 7° isosteres as continuous lines. The figures placed at the ends of the isosteres represent total adsorption in mM/g.

Over the whole range of pressures studied, the total adsorption isosteres for the system C_2H_4–C_3H_6 are, within the limits of experimental accuracy and of the error of interpolation, straight lines for both temperatures, the slope of the lines gradually rising with increase in the degree of filling up of the active surface. This empirical relationship was also found in the previously studied system, CO_2–C_2H_4, for which the total adsorption isosteres were also straight lines; from our point of view this is of considerable interest, and has been found to hold for both gaseous mixtures studied by us. Papers on adsorption of mixtures of gases published during the past few years [3-6] are neither detailed enough nor sufficiently accurate to allow us to make use of these data for checking the linearity of total adsorption isosteres.

If this empirical relationship turns out to be a not special case, but to be of more general applicability, at least for the case of low degrees of filling up of the active surface, it would be of importance, inasmuch as it would permit the construction of the total adsorption surface from the adsorption isotherms of the individual

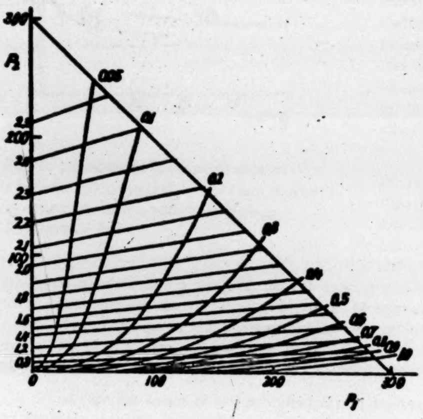


Fig. 4. Family of adsorption isosteres for propylene a_2 = const. (straight lines) from 0.6 to 2.5 mM/g, and of isosteres for ethylene (curved lines) from 0.05 to 1.0 mM/g. The axes represent partial pressures of ethylene (p_1) and propylene (p_2) in mm.

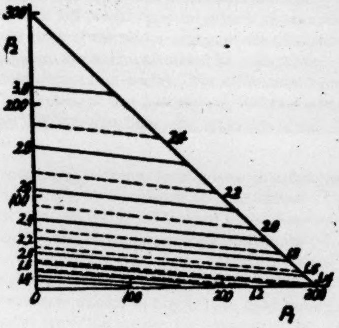


Fig. 5: Family of total adsorption isosteres for ethylene and propylene $a_{12} = a_1 + a_2$ = const., from 1.2 to 3.0 mM/g, at 7°(continuous lines), and from 1.2 to 2.4 mM/g, at 25° (broken lines). The coordinates are partial pressures of ethylene (p_1) and propylene (p_2), in mm.

components. If the total adsorption isosteres are straight lines, then the construction therefrom of total adsorption surfaces should be very simple. It should be enough to plot on the coordinate planes $p_2 = 0$ and $p_1 = 0$ the adsorption isotherms of the individual components of the mixture $a_1^0 = f_1(p_1, 0)$ and $a_2^0 = f_2(p_2, 0)$, and then to imagine that along these two isotherms, as if along rails, a third straight line, parallel to the coordinate surface $a_i = 0$, is slid. The surface traced by the movement of this line will be the total adsorption surface.

The constancy of the coefficient α in the sections for constant total degree of saturation of the surface was noted above. It is evident that in every such section the curves $a_1 = f_1(p_1, p_2)$ and $a_2 = f_2(p_1, p_2)$ at a_{12} = const. will be represented by hyperbolic equations, fully determined by the parameter α. Hence if we could in any way find the nature of the dependence of α on the degree of saturation of the active surface this should, on the condition of the linearity of the total adsorption isosteres, be sufficient for the construction of the surfaces $a_1 = f_1(p_1, p_2)$, $a_2 = f_2(p_1, p_2)$, and $a_{12} = a_1 + a_2$ from the isotherms of adsorption of the individual components. We shall return to this question in the next part of this series.

The following illustrates how closely linear are the total adsorption isosteres for the system C_2H_4–C_3H_6. After completing the measurements of adsorption of the mixtures, and the working out of the experimental results, the isosteres of Fig. 5 were produced, to cut the p_1 axis, thus giving a series of extrapolated points on the adsorption isotherm for pure ethylene; the extrapolation was continued up to a pressure of 760 mm. Direct measurements of adsorption of ethylene at 25° and at pressures of up to 760 mm were then made, and the points so obtained were found to lie satisfactorily on the extrapolated curve above.

5. Certain Thermodynamic Considerations

Measurements of simultaneous adsorption of ethylene and propylene were made at two different temperatures, with the object of elucidating the nature of the changes in differential heat of adsorption of each component of the mixture. As is well known, the differential heats of adsorption of a single substance can be derived by the Clausius-Clapeyron equation from the adsorption isosteres, or approximately from two adsorption isotherms at two different temperatures. The differential heats of adsorption of each component were thus calculated, for different values of the degree of saturation of the active surface.

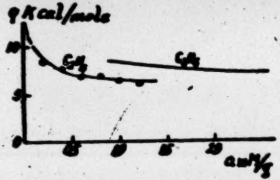


Fig. 6. Differential heats of adsorption of ethylene and propylene, in relation to degree of saturation of the adsorbent surface
1) q kg-cal/mole

Fig. 6 shows the curves relating differential heats of adsorption of ethylene and propylene to magnitude of adsorption. Owing to the steep slope of the initial section of the adsorption isotherms for propylene, the heats calculated for adsorptions less than 1.0 mM/g are not trust-worthy. The differential heat of adsorption q of ethylene at first falls steeply, and then more gradually, almost linearly, with increasing saturation of the adsorbent surface.

From the adsorption isotherms for ethylene we calculated the change in free energy, by integrating from the Gibbs' equation, and we then calculated the integral heats of adsorption Q at different degrees of saturation of the surface, by substituting in equations of the type of (2). Graphical differentiation of the curve Q = Q(a) so obtained gave the differential heats of adsorption $q = \partial Q/\partial a$; the values so obtained are represented by circles on Fig. 6. The good agreement found between the values of q calculated by two methods is evidence of the satisfactory accuracy of the calculation of change in free energy from the adsorption isotherms for ethylene. Similar calculations for propylene are, unfortunately, as little trustworthy as are the calculations of heats of adsorption from two adsorption isotherms.

We are not aware of any published papers dealing with the calculation of differential heats of adsorption of mixtures of gases, for which reason we think that the matter merits a detailed consideration. The integral heat of adsorption of a binary mixture of gases Q_v can obviously be derived from the equation

$$-Q_v = U = F - T\left(\frac{\partial F}{\partial T}\right)_{v,\, a_1,\, a_2}, \tag{2}$$

in which U is the change in internal energy, F is the change in external energy, and V is the volume of the system.

In order to calculate Q_v from equation (2) it is necessary to find F and $(\partial F/\partial T)_{v,\, a_1,\, a_2}$ from Gibbs' equation (3):

$$dF = RTa_1 d\ln p_1 + RTa_2 d\ln p_2, \tag{3}$$

in which we shall, for the sake of simplicity, put pressure instead of fugacity.

Applying to equation (3) the formula for differentiating by parts, in order to change from the independent variables p_1 and p_2 to the independent variables a_1 and a_2, and integrating the equation so obtained from zero along the path $a_2 = 0$ to some value of a_1, and then along the path a_1 = const. to the point (a_1, a_2), we obtain the change in free surface energy associated with adsorption of a_1 moles of the first and a_2 moles of the second component on an initially free surface. By calculating the partial derivative $(\partial F/\partial T)_{v,a_1,a_2}$ and substituting these values in equation (2) we obtain the following expression for Q_v

$$Q_v = \int_0^{a_1} RT^2 \left[\frac{\partial \ln p_1(a_1, 0)}{\partial T}\right]_{v,a_1,a_2} da_1 + \int_0^{a_2} RT^2 \left[\frac{\partial \ln p_2(a_1, a_2)}{\partial T}\right]_{v,a_1,a_2} da_2. \tag{4}$$

Since the first term of the right-hand side of equation (4) is the integral of the heat of adsorption of the first component along Q_1^0 we can, omitting the subscript v, write the equation in the form

$$Q = Q_1^0 + \int_0^{a_2} RT^2 \left[\frac{\partial \ln p_2(a_1, a_2)}{\partial T}\right]_{a_1,a_2} da_2 \tag{5a}$$

Integrating at first along the path $a_1 = 0$, and then along the path a_2 = const. to the point (a_1, a_2) we obtain the completely analogous equation

$$Q = Q_2^0 + \int_0^{a_1} RT^2 \left[\frac{\partial \ln p_1(a_1, a_2)}{\partial T}\right]_{v,a_1,a_2} da_1, \tag{5b}$$

where Q_2^0 is the integral heat of adsorption of the second component alone.

Equations (5a) and (5b) serve for derivation of the integral heat evolved during the simultaneous adsorption of a_1 moles of the first, and a_2 moles of the second component of the mixture.

Differentiating equation (5a) with respect to a_2 and equation (5b) with respect to a_1, we obtain the differential heat of adsorption of each component adsorbed simultaneously:

$$\left.\begin{aligned} q_1 &= \left(\frac{\partial Q}{\partial a_1}\right)_{a_2} = RT^2\left[\frac{\partial \ln p_1(a_1,a_2)}{\partial T}\right]_{a_1,a_2} \\ q_2 &= \left(\frac{\partial Q}{\partial a_2}\right)_{a_1} = RT^2\left[\frac{\partial \ln p_2(a_1,a_2)}{\partial T}\right]_{a_1,a_2} \end{aligned}\right\} \tag{6}$$

Representing the differential heat of adsorption of a mixture of the composition (N_1, N_2) by q_{12}, we obtain

$$q_{12} = N_1 q_1 + N_2 q_2. \tag{7}$$

For a mixture of the equilibrium composition $N_1 = p_1 / P$, $N_2 = p_2 / P$, $P = p_1 + p_2$ etc., whence

$$q_{12} = \frac{p_1}{P}\ RT^2\left(\frac{\partial \ln p_1}{\partial T}\right)_{a_1,a_2} + \frac{p_2}{P}\ RT^2\left(\frac{\partial \ln p_2}{\partial T}\right)_{a_1,a_2} = RT^2\left(\frac{\partial \ln P}{\partial T}\right)_{a_1,a_2} \tag{8}$$

On the basis of the families of isosteres of adsorption of both components at two different temperatures we calculated, using equation (6) the differential heats of adsorption of ethylene q_1 and propylene q_2 from mixtures of the two gases; the results are represented in Figs. 7 and 8.

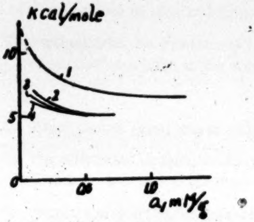


Fig. 7. Differential heats of adsorption of ethylene q_1 depending on adsorption of ethylene a_1 at constant values of a_2: 1) a_2 = 0; 2) a_2 = 1.0; 3) a_2 = 1.4; 4) a_2 = 1.6.

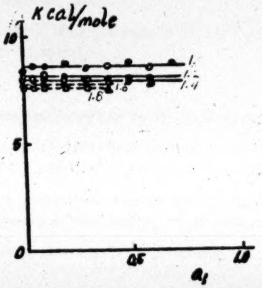


Fig. 8. Relation between differential heats of adsorption of propylene q_2 and adsorption of ethylene a_1 at constant values of a_2. The figures placed at the ends of the curves relate to adsorption of propylene in mM/g.

Fig. 7 shows the dependence of the differential heat of adsorption of ethylene q_1 on the amount of adsorption a_1, at various constant values of adsorption of propylene a_2. It is evident from this graph that the presence of propylene in the adsorbed phase causes considerable diminution in the differential heat of adsorption of ethylene. In other words, the propylene molecules occupy the parts of the surface which have the greatest values for energy of adsorption, and under these conditions the ethylene molecules are in general adsorbed on those parts of the surface which have lower (and more uniform) values of energy of adsorption than when ethylene alone is adsorbed. From our point of view, this fact is in full agreement with the widening of the Henry region of the adsorption isotherms of ethylene in the presence of propylene.

Fig. 8 shows the relation between differential heats of adsorption of propylene q_2 and the amount of adsorption of ethylene a_1, at constant values of a_2. With a_2 = const. the heat of adsorption of propylene is practically independent of the ethylene content of the adsorbed phase, and falls only very gradually with increase in the propylene content. Thus the presence of ethylene does not interfere with adsorption of propylene molecules on the parts of the surface giving higher values of adsorption energy.

It is of considerable interest for the thermodynamic analysis of the properties of the adsorbed phase to know the partial values for change in free surface energy, i.e., the partial two-dimensional pressures. It should be noted that Rowley and Innes have published a series of papers [6] on the thermodynamics of adsorption of mixtures, dealing in particular with changes in free surface energy associated with this process. Their analysis of these variations seems, however, to be valueless to us, since it is based on a gross thermodynamic error. If we integrate equation (3) we obtain:

$$\Delta F = s\pi = \int_0^{p_1} RTa_1 d\ln p_1 + \int_0^{p_2} RTa_2 d\ln p_2 \qquad (9)$$

(here π is two-dimensional pressure, and $\underline{s}$ is specific surface of the adsorbent). The sum of the two integrals of the right-hand side of this equation does not, of course, depend on the path of integration, since this sum gives the change in the function of state. It is, however, quite unreasonable to assume, as do Innes and Rowley, that each integral can sepaately be considered as a change in some function of state, and to call it the partial two-dimensional pressure of the given component. On the contrary, it can readily be shown that, taken separately, these integrals depend on the path of integration. For this reason, the thermodynamic conclusions drawn by Rowley and Innes from this are meaningless.

It might have been possible, having calculated the total two-dimensional pressure from formula (9) to assume, by analogy with the three-dimensional case, that $\pi_i = N_i^{\sigma} \cdot \pi$, but with quite considerable deviations from ideality, such as appear to be the rule in the surface layer, such a determination could have only a purely formal value. It would be of considerable interest to determine the partial two-dimensional pressure in an analogous way to that applied by Temkin [7] to grossly non-ideal three-dimensional systems. In that case, however, we would require accurate measurements of adsorption, down to very small degrees of saturation of the active surface, which we have not done. These considerations oblige us, at the present time, to abstain from attempting an analysis of the equations of state of binary adsorption layers.

The authors take this opportunity to express their gratitude to M. M. Dubinin and B. V. Ilyin for their unfailing interest and assistance in the present research.

SUMMARY

1. Simultaneous adsorption of ethylene and propylene on active charcoal has been studied, at 7° and 25°.

2. The adsorption surfaces found greatly resemble those reported in an earlier paper for simultaneous adsorption of carbon dioxide and ethylene on the same sample of active charcoal.

3. Families of adsorption isosteres are constructed for each component separately and for both together, and the projections of the total adsorption isosteres on the plane $a_i = 0$ are shown to be straight lines.

4. The selectivity coefficient is shown to be constant in the section of constant total saturation of the active surface.

5. Formulas are derived for integral and differential heats of adsorption of the components from mixtures of gases. These formulas are used to calculate the partial differential heats of adsorption.

6. The question of partial two-dimensional pressures in a binary adsorption layer is considered, and a gross thermodynamic error made by Innes and Rowley is pointed out.

Received May 27, 1952

Institute of Physical Chemistry
Academy of Sciences USSR and
M. V. Lomonosov Moscow State University

LITERATURE CITED

[1] B. P. Bering and V. V. Serpinsky. J. Phys. Chem. 26, 253 (1952).

[2] J. Senderens, Comptes. rend. 190, 1167 (1930).

[3] J. Arnold, J. Am. Chem. Soc. 71, 104 (1949).

[4] W. Lewis, E. Gilliland, B. Chertow and coworkers, Ind. Eng. Chem. 42, 1319 (1950); J. Am. Chem. Soc. 72, 1153, 1157, 1160 (1950).

[5] F. Tompkins, D. Young, Trans. Faraday Soc. 47, 88 (1951).

[6] W. Rowley, R. Olney, W. Innes, J. Am. Chem. Soc. 72, 5180 (1950); J. Phys. Coll. Chem. 55, 1324 (1951).

[7] M. L. Temkin, Acta. Phys. Chim. USSR 20, 713 (1945).

STUDIES OF CAPILLARY CONDENSATION OF VAPORS IN HIGHLY DISPERSE SYSTEMS

PART 1. CALCULATION OF CAPILLARY CONDENSATION IN THE VICINITY OF POINTS OF CONTACT OF SPHERICAL PARTICLES

L. V. Radushkevich

The study of capillary condensation of vapors in highly disperse systems is of both theoretical and practical importance, in view of the wide distribution of such systems, and of their frequent practical application. It is generally believed that capillary condensation of vapors takes place in the fine pores of highly disperse substances as a result of the lowering of vapor pressure over the concave meniscus of the liquified substance. Papers have been published [1-3] dealing with this effect, and connected with the verification of the Thomson-Kelvin equation. However, in spite of the numerous studies in this direction, and of discussions of the deviations from the equation found, these papers cannot be considered to be entirely satisfactory. It appears to us that up to now the question has not been clearly enough defined, from the physical point of view. The quantitative description of the process in ordinary porous substances involves a number of arbitrary assumptions regarding the shape of the pores, which is assumed to be simple, although it is generally known that the structure of pores is as a rule complex. In those cases in which the workers dealt with pores of a definite shape, as in the researches of Shereshefsky [2] and Chmutov [3], they avoided the study of the process taking place in porous substances, and did not possess sufficient information regarding the structure of the walls of their artificially formed capillaries and fissures.

Incidentally, the problem of capillary condensation in an artificial fissure formed between a convex lens and a plane surface, which was solved by Chmutov [3], seems to us to be the most promising, inasmuch as it introduces the idea of the process in the vicinity of the point of contact. Continuing this line of thought, we arrive at the concept of condensation of vapors on contiguous bodies, in general, as well as at the special case of condensation in systems consisting of numerous small particles in contact with each other. To such systems would belong various powders, and precipitates of highly disperse substances. In those cases in which the size and shape of the particles are known sufficiently well, and in which measurements of adsorption have shown that capillary condensation pores are absent from the individual particles, the systems are the most suitable for the study of capillary condensation. They are of interest both as models, and for their intrinsic importance, and are particularly suitable for the solution of the problems when the constituent particles have some simple shape.

Certain varieties of soot fulfill these requirements. Electronmicroscope studies of certain soot particles show that they are of spherical form; these findings are beyond doubt, and have been confirmed by numerous authors [4], although no explanation has been advanced as to why they have so simple a shape. Moreover, the size of the particles is quite small, most of them being between 200 and 2000 A in diameter. A further advantage is that the particles of most specimens of soot have been shown by adsorption measurements not to be porous. Fig.1** is an electron-photomicrograph of a specimen of lamp-black P-33, prepared by D. G. Kadaner, which shows clearly the spherical shape of the particles. According to Emmett and De Witt and other authors [4] the specific surface of this variety of soot is about 20 m^2/g as shown by measurements of adsorption of nitrogen. Its geometrical specific surface, derived from measurements of electron-photomicrographs, is 19.4 m^2/g. It may hence be accepted that the individual spherical particles of this material do not in fact possess pores in which additional capillary condensation of vapors could proceed. It is evident from Fig. 1 that the particles are of different sizes, i.e., the system is a polydisperse one. Other varieties of soot are, however, known in which the particle size is practically uniform.*

Capillary condensation of vapors takes place around the numerous points of contact of the particles of compressed pellets of soot; the shape of the crevices between the particles can be known with sufficient accuracy.

---

* The possibility of capillary condensation in non-porous soots was shown by V. M. Lukyanovich. Spherical particles were also found in aerosols of oxides of metals.

** See page 894.

Each pair of spheres forms a sorption cell, or condensation center, in which appearance of the first portions of liquified vapor leads, on condition of wetting of the surface, to formation of a concave meniscus, and this leads to the development of the process of capillary condensation.

1. General description of the problem

The simple shape of the particles and of the crevices formed between them permit an exact consideration of the process of condensation, without involving any doubtful assumptions regarding the shape of the pores. We can thus, for a sorption cell consisting of spherical particles, undertake to a certain extent "classical" derivation of the capillary condensation isotherms from the Thomson-Kelvin equation. Experimental evidence of the absence of pores in the individual particles render such calculations fully justifiable.

The research consisted of the following. We first calculate capillary condensation for an elementary sorption cell, consisting of two spheres in contact, taking into account measurements of vapor pressure and of corresponding changes in the curvature of the surface of the meniscus. The transition from the elementary cell to a monodisperse system is then made; this system consists of a large number of spheres in contact with each other, and it may be assumed in the simplest case that they are packed in an orderly manner. The full calculation of the capillary condensation isotherm is possible for such a system. This simple model may serve for the discovery of certain general features of the process of condensation of vapors in systems formed of small contiguous particles, and a number of useful generalizations applying to more complex systems of this sort may be made.

The relation between the curvature of the surface and the vapor pressure of a liquid is given by the classical Thomson-Kelvin equation. We initially applied this relation without taking into account deviations from the equation sometime observed during experiments. We believe that with a fully developed condensation process all the deviations can be ascribed only to imperfect knowledge of the surface tension and the molar volume of the liquids. We do not, for this reason, study the process at low relative pressures p/p_s, at which the deviations may assume large proportions, but we confine our analysis of the process to saturations roughly from $p/p_s = 0.5$ to full saturation ($p/p_s = 1$).

The very small radius of the spheres of which our highly disperse systems are made up is very characteristic of them. A consequence of this feature is that we must, in general, in calculating the curvature of the annular meniscus formed around the point of contact of the two spheres of the adsorption cells, take into account the double curvature of the surface, since in the given case both radii of curvature are very small at any point in the meniscus, and are of the same order of magnitude. Under conditions of full wetting the Thomson equation takes the following form, for an adsorption cell:

$$1/\rho + 1/\rho^* = \frac{R_s T \ln p_s/p}{\sigma V} = \frac{2}{C}, \qquad (1)$$

where ρ and ρ^* are the radii of curvature of the surface of the meniscus, σ is the surface tension of the liquid, V is the molar volume, R_s is Clapeyron's constant, and T is absolute temperature.

The constant C in equation (1), expressed by the relation

$$C = \frac{2\sigma V}{R_s T \ln p_s/p}, \qquad (2)$$

has a simple physical sense; it is the radius of curvature of the annular meniscus of the liquid, equivalent to the given capillary cell.

We shall in the future assume full wetting, although there would be no particular difficulty in calculating the angle of contact. Since capillary condensation on spherical particles is always preceded (at low relative pressures) by formation of a monomolecular adsorption layer covering the whole surface, the assumption of full wetting corresponds more closely to reality.

2. Capillary condensation in a sorption cell, for the limiting case.

The volume of condensed liquid around the point of contact of two spheres of equal radius can readily be calculated for the limiting case of full saturation, i.e. when the relative vapour pressure p/p_s is equal to unity. The condition $p/p_s = 1$ leads to a value of $C = \infty$ in the preceding formulas, and in this case the Thomson equation assumes the simple form:

$$1/\rho + 1/\rho^* = 0. \qquad (3)$$

It hence follows that the meniscus of the liquid around the point of contact of the spheres corresponds to a surface of rotation of zero curvature. It is well known that such a surface is a catenoid, obtained by the rotation of a section of a catenary curve around some axis.

The point of intersection of the coordinates is given by the point of contact of the spheres (Fig. 2), taking as the x axis a line joining the centers of the spheres, and as the y axis a line perpendicular to this. In these circumstances the equation of the catenary curve NM is:

$$y = a \operatorname{ch} x/a.$$

In order to find the volume of condensed liquid it is necessary to determine the parameter a of this curve, as well as the coordinates x_M and y_M of one of the points of contact of the catenary with a sphere (point M). It follows from the condition $C = \infty$ that the values of a, x_M, and y_M depend only on the radius of the sphere, R, and not on any material constant.

The equation for a segment, the center of which is on the x axis, and which touches the y axis at its origin, has the form:

$$y = \pm \sqrt{2Rx - x^2}.$$

If the condition of full wetting is accepted, then it is obvious that the catenary must contact the sphere at the point M, on the conditions that

$$\left.\begin{aligned} a \operatorname{ch} x_M/a &= \sqrt{2Rx_M - x_M^2} \\ \operatorname{sh} x_M/a &= \frac{R - x_M}{a \operatorname{ch} x_M/a} \end{aligned}\right\} \quad (4)$$

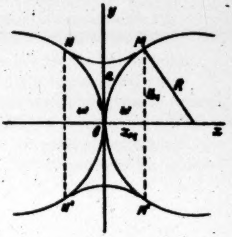


Fig. 2

If for convenience we write $z_0 = R/a$ and $z = x_M/a$, equation (4) takes the form

$$\operatorname{ch} z = \sqrt{2zz_0 - z^2} \quad (5)$$

and

$$\operatorname{sh} 2z = 2(z_0 - z). \quad (6)$$

The second of these gives

$$z_0 = z + {}^1/_2 \operatorname{sh} 2z. \quad (7)$$

Eliminating z_0 from formulas (5) and (7) we obtain the transcendental equation for the unknown z:

$$\operatorname{sh} 2z = \frac{\operatorname{ch}^2 z}{z} - z, \quad (8)$$

which has one real root, and may readily be solved graphically. We thus find that $z = 0.639$, after which equation (7) gives $z_0 = 1.468$. The value of the parameter a of the catenary can hence readily be calculated, as well as the coordinates of the point M:

$$a = \frac{R}{1.468} = 0.681 \cdot R; \; x_M = 0.681 \cdot 0.639R = 0.436R; \; y_M = 0.826R.$$

As was expected, all three characteristics of the geometric conditions for formation of the meniscus are proportional to the radius R. The volume v of the liquid between the two contiguous spheres is obviously equal to that of the catenoid NMN'M' (Fig. 2), less twice the volume of the included segment of the sphere, i.e., $v = V_K - 2w$.

The volume V of the catenoid is given by

$$V_K = {}^1/_2 \; \pi a^3 \left(\operatorname{sh} \frac{2x_M}{a} + \frac{2x_M}{a}\right). \quad (9)$$

The values of a and x_M were derived by us above, as fractions of the radius of the spheres, whence it follows that $2x_M/a = 1.279$, and that $V_K = \frac{1}{3}\pi\ (0.681)^3 \cdot R^3$ (sh 1.279 + 1.279) or $V_K = 0.4640\pi R^3$.

The volume w of the segment of the sphere, height x_M and half-chord length y_M is given by $w = \frac{1}{6}\pi x_M(3y_M^2 + x_M^2)$. Substituting the values of x_M and y_M found by us we obtain $2w = 0.3244\pi R^3$. The volume of liquid formed around the point of contact is thus finally given by $v = V_K - 2w = \pi R^3(0.4640-0.3244)$, or

$$v = \frac{2}{3}\pi R^3 \cdot 0.2094 \qquad (10)$$

It hence follows that v is proportional to the volume of the contiguous spheres, the coefficient of proportionality being independent of the properties of the liquid or vapor.

We would add that the value of the volume obtained above corresponds with limiting filling of the sorption cell formed by two contiguous spheres. The total amount of capillary-condensed liquid per unit mass of sorbent will be calculated below.

3. Shape and parameters of the meniscus of the liquid obtained by capillary condensation of vapor in a sorption cell (general case).

The above case of limiting filling of a sorption cell formed of two contiguous spheres is that obtained at completion of the process of capillary condensation of vapor in crevices. We were able to show that this state is associated with formation of a concave liquid meniscus of definite shape and dimensions which are independent of the nature of the adsorbate (of its physical constants). The effect of the nature of the vapor undergoing condensation is manifested in the process of filling up of the cells. It is not yet possible to follow the development of the process of condensation with time, i.e., the kinetics of capillary condensation. We cannot for this reason describe the process of appearance of the first portions of liquid around the point of contact, but in general it may be supposed that the process of increase in the amount of condensed vapor, as the equilibrium pressures rise from small to high values, can be represented as a progressive shift of the concave equilibrium meniscus farther and farther from the point of contact. To each relative pressure p/p_s will correspond a given liquid meniscus and a definite volume of liquid in the cell. At the limit, when $p/p_s = 1$, the amount of liquid in the cell will be at a maximum.

We shall now determine the shape of the meniscus and its parameters for the case $p/p_s < 1$, in order to ascertain how the amount of capillary condensed liquid in a cell gradually rises with increasing p/p_s, and thence to construct isotherms of capillary condensation. Under these conditions the magnitude C is finite $(C > 0)$, and the problem reduces itself, in the first place, to an analysis of an equation of the type:

$$1/\rho + 1/\rho^* = \frac{2}{C}. \qquad (11)$$

For p/p_s = const. the equation corresponds to the surfaces of a constant final curvature. It is known [5] that one such surface is the so-called nodoid, obtained by the rotation of a flat spiral line (trochoid) around some axis. A second surface with a constant curvature is the unduloid, given by the rotation of an undulating line around a specific axis.

The problem of finding the shape and the parameters of the meniscus of the liquid between contiguous spheres can be solved, in its most general form, one of the solutions corresponding to a concave mensicus, and another to a convex meniscus. It is evident that the second case is connected with the theoretical description of the process of evaporation.

The equation for the meridianal curve of the figure of rotation forming the meniscus of the liquid can be derived in the following way. Let AB (Fig. 3) be an arc of the meridianal curve, the axis of rotation of which coincides with the line zz'. We shall adopt the arbitrary convention that the direction on the axis z from below up is a positive one, and the abscissas axis or will be drawn through the point of contact of the spheres. c and c' are the centers of curvature of the surface, corresponding with the radii of curvature ρ and ρ^* at any point of this surface of rotation. It is evident from the figure that

$$\frac{1}{\rho^*} = \frac{\sin\tau}{r} \quad \text{and} \quad \frac{1}{\rho} = \frac{p}{(1+p^2)^{3/2}},$$

where $p = dz/dr$.

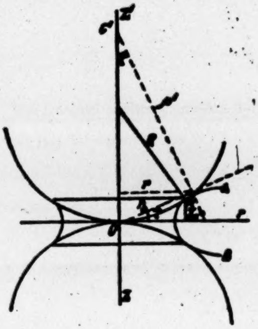


Fig. 3

It is also obvious that $\frac{d}{dr}\sin\tau = \frac{d}{dr}\frac{p}{\sqrt{1+p^2}} = \frac{p'}{(1+p^2)^{3/2}} = \frac{1}{\rho}$. The left-hand side of equation (11) can thus be written in the form

$$\frac{1}{\rho} + \frac{1}{\rho'} = \frac{d}{dr}\sin\tau + \frac{\sin\tau}{r}$$

or

$$\frac{1}{\rho} + \frac{1}{\rho'} = \frac{1}{r}\frac{d(r\sin\tau)}{dr}.$$

Consequently

$$\frac{1}{r}\frac{d(r\sin\tau)}{dr} = \frac{2}{C}\,. \qquad (12)$$

in which $C > 0$.

Equation (12) is the basic differential equation for the derivation of the shape of the meridianal curve. The first integration gives:

$$r\sin\tau = \frac{r^2}{C} + \text{const.} \qquad (13)$$

In considering how to find the value of the integration constant it should be noted that for all the diverse cases of the meniscus of the liquid between two contiguous spheres the angle τ of slope of the tangent to the or axis may assume any values, since otherwise an additional condition, devoid of any physical meaning, in the given case, would have to be imposed on formation of the meniscus. We know that of the two meridianal curves giving surfaces of constant curvature the undulant curve corresponding to an unduloid has inflection points with finite values of τ, and does not have any points at which $\tau = 2\pi n$. On the other hand, a trochoid has no points of inflection, and for it τ can have any values. These considerations show that in the given case a trochoidal meniscus is formed (in the general case it is convex or concave).

Analysis of equation (13) shows that the variable r varies between the minimum and maximum values. In fact, $\sin\tau$ varies between the limits -1 to $+1$. For these cases we have

$$-r_1 = \frac{r_1^2}{C} + \text{const.} \qquad (14)$$

and

$$+r_2 = \frac{r_2^2}{C} + \text{const.} \qquad (15)$$

where r_1 and r_2 are the minimum and maximum distances of the trochoid from the zz' axis. It follows from these equations that

$$r_2 - r_1 = C. \qquad (16)$$

It is further clear that the value of the angle $\tau = (2n+1)\pi/2$ corresponds to that of a concave meniscus, the examination of which is our object. For this meniscus on the or axis a distance of the trochoid from zz' of $r = r_1$, is the minimum one. At $\tau = 2n\pi/2$ the value of r achieves a maximum value of r_2, which corresponds to a convex meniscus. The trochoid is thus characterized by two parameters r_1 and r_2, which are connected with C as in equation (16). Since in our problem C is known, we need determine only the parameter r_1.

Substituting the value of the integration constant from equation (14) into equation (13) we obtain

$$\sin\tau = 1/C\left(r - \frac{r_1^2}{r}\right) - \frac{r_1}{r} = \frac{p^2}{\sqrt{1+p^2}}.$$

Solving this equation for $p = dz/dr$ we obtain

$$\frac{dz}{dr} = \pm\frac{r_1 r_2 - r^2}{\sqrt{(r^2 - r_1^2)(r_2^2 - r^2)}} \qquad (17)$$

where the upper sign corresponds to the positive direction taken by us on the z axis. It should be noted that in our problem $r_1 r_2$ is always $> r^2$, since the values of r which concern us are close to r_1.

We obtain from equation (17), on the condition that $\underline{z} = 0$ for $\underline{r} = \underline{r_2}$:

$$z = \pm \int_{r_1}^{r} \frac{r_1 r_2 - r^2}{\sqrt{(r^2 - r_1^2)(r_2^2 - r^2)}}\, dr. \tag{18}$$

The integral of this expression is converted in the usual way into elliptic integrals of the 1st and 2nd orders. Writing for convenience

$$\Delta\phi = \sqrt{1 - K^2 \sin^2\phi} \tag{19}$$

and assuming that

$$r = r_2 \cdot \Delta\phi, \tag{19^I}$$

where $\underline{K}$ is a modulus, and ϕ is the argument of the elliptic integrals. We know that

$$K = \sin\alpha = \sqrt{\frac{r_2^2 - r_1^2}{r_2^2}}. \tag{19^{II}}$$

We then obtain, after substitution of the variables in formula (18):

$$z = \pm\, [r_1 \Phi(\alpha, \phi) - r_2\ \Psi(\alpha, \phi)]. \tag{20}$$

We have here, for the sake of shortness, assumed

$$\left.\begin{aligned} \Phi(\alpha, \phi) &= F(\alpha) - F(\alpha, \phi) \\ \Psi(\alpha, \phi) &= \mathcal{E}(\alpha) - E(\alpha, \phi) \end{aligned}\right\} \tag{20^I}$$

where $F(\alpha)$ and $\mathcal{E}(\alpha)$ are full elliptic integrals of the 1st and 2nd orders, in the Legrange form:

$$\left.\begin{aligned} F(\alpha) &= \int_0^{\pi/2} \frac{d\phi}{\Delta\phi} \\ \mathcal{E}(\alpha) &= \int_0^{\pi/2} \Delta\phi \cdot d\phi \end{aligned}\right\} \tag{21}$$

The functions $F(\alpha, \phi)$ and $E(\alpha, \phi)$ are elliptic integrals of the first and second orders, from the argument ϕ:

$$\left.\begin{aligned} F(\alpha, \phi) &= \int_0^{\phi} \frac{d\phi}{\Delta\phi} \\ E(\alpha, \phi) &= \int_0^{\phi} \Delta\phi d\phi \end{aligned}\right\} \tag{22}$$

Formula (20) is the equation for the required meridianal curve, which is an infinite flat spiral line (trochoid), with the parameters r_1 and r_2. We are concerned with only a small section of the trochoid near the point with the abscissa r_1, to which corresponds the concave meniscus of the liquid. The integrals (21) and (22) are tabulated [6]. We have prepared auxiliary tables for the differential integrals Φ and Ψ, entering into formula (20).

The problem of finding the parameters of the trochoid meniscus may be formulated as follows: to make a section of the trochoid for a given value of $\underline{C}$, symmetrically in contact with two contiguous circles of radius $\underline{R}$. The point of contact of the circles is at the point of intersection of the coordinate axes (Fig. 3), and the centers of the circles are on the $\underline{z}$ axis. As a result of the symmetry of the system around the $\underline{r}$ axis the problem may be simplified, and reduced to the derivation of the parameters of a trochoid touching one of the circles, the point of a trochoid with the abscissa $\underline{r_1}$ lying on the $\underline{r}$ axis. We let this contact take place at the point $\underline{M}$, having the coordinates r_0 and z_0. The equation for the circumference will have the form

$$z = R \pm \sqrt{R^2 - r^2}.$$

We have for the point of contact $\underline{M}$, under conditions of full wetting:

$$R - \sqrt{R^2 - r_0^2} = r_1 \Phi(\alpha, \phi_0) - r_2 \Psi(\alpha, \phi_0) \tag{23}$$

$$\frac{r_0}{\sqrt{R^2 - r_0^2}} = \frac{r_1 r_2 - r_0^2}{\sqrt{(r_0^2 - r_1^2)(r_2^2 - r_0^2)}} \tag{24}$$

In addition, we have the relation

$$C = r_2 - r_1. \tag{25}$$

In the system of equations (23),(24), and (25) the values of r_1, r_2, and r_0 are unknown. Obviously $r_2 > r_0 > r_1$.

From equation (24) we find

$$r_0 = \sqrt{\frac{R r_1 r_2}{R + C}}\ . \tag{26}$$

We introduce the non-dimensional magnitudes

$$\beta = C/R;\ x = r_1/R;\ x + \beta = r_2/R;\ x_0 = r_0/R$$

Formula (26) then takes the form

$$x_0 = \sqrt{x \frac{x + \beta}{1 + \beta}}\ . \tag{26$^{\text{I}}$}$$

After substituting the new values and the value of x_0 in formula (23) we obtain

$$1 - \sqrt{1 - x\frac{x + \beta}{1 + \beta}} = x\,[\Phi(\alpha, \phi_0) - \Psi(\alpha, \phi_0)] - \beta\,\Psi(\alpha, \phi_0). \tag{27}$$

It follows from equations (19), (19$^{\text{I}}$), and (19$^{\text{II}}$) that

$$\sin \alpha = \sqrt{1 - \left(\frac{x}{x + \beta}\right)^2} \tag{28}$$

$$\sin \phi_0 = \frac{1}{\sin \alpha}\sqrt{1 - \frac{\cos \alpha}{1 + \beta}}\ . \tag{29}$$

Equation (27) is solved graphically, at the given value of β. Its right-hand side is a function of $\underline{x}$ only, since the angles α and ϕ_0 depend on $\underline{x}$, according to equations (28) and (29). The graphical construction shows that for each value of β equation (27) has only one root, i.e., $\underline{x}$ is determined unambiguously.

We shall here outline the solution in principle only. In practice, since the published tables give values of elliptic integrals at different moduli at 5° intervals, and for arguments at 1° intervals, we applied this method, in order to avoid laborious interpolations.

It follows from (28) that $\underline{x} = \beta \cdot \eta$, where $\eta = \dfrac{\cos \alpha}{1 - \cos \alpha}$; the lefthand side of equation (27) then assumes the form:

$$P_1(\eta) = 1 - \sqrt{1 - \beta^2 \frac{\eta(\eta + 1)}{1 + \beta}}; \tag{27$^{\text{I}}$}$$

and the right-hand side will be:

$$P_2(\eta) = \beta\left\{\eta\,[\Phi(\alpha, \phi_0) - \Psi(\alpha, \phi_0)] - \Psi(\alpha, \phi_0)\right\} \tag{27$^{\text{II}}$}$$

Using the tables, we construct a family of curves for $\Psi(\alpha, \phi_0)$ and $\Phi(\alpha, \phi_0) - \Psi(\alpha, \phi_0)$ in relation to ϕ_0, at values of α through 5° to 85°. All values of η were calculated for each given β, as well as the corresponding values of the angle ϕ_0, from the formula (29). We then used formulas (27$^{\text{I}}$) and (27$^{\text{II}}$) for the calculation of the functions $P_1(\eta)$ and $P_2(\eta)$, and graphs were drawn, in which the values of the roots η at different β were given by the points of intersection. The unknowns $\underline{x}$ were finally derived from the relation $\underline{x} = \beta\eta$.

We thus found the values of $\underline{x}$ and $x + \beta$ for a series of values of the parameter, and we then derived the values of $\underline{x_0}$ from formula (26$^{\text{I}}$), i.e., we achieved a full solution of the problems of the parameters of the meridianal curve, which is the concave meniscus of the liquid between two contiguous spheres. The results of these calculations are given in Table 1.

TABLE 1

$\beta = C/R$	$x = r_1/R$	$x_0 = r_0/R$	$x + \beta = r_2/R$
0.05	0.194	0.212	0.244
0.10	0.250	0.282	0.350
0.20	0.325	0.377	0.525
0.30	0.370	0.437	0.670
0.40	0.404	0.482	0.804
0.50	0.432	0.518	0.932
0.60	0.455	0.548	1.055
0.80	0.485	0.588	1.285
1.00	0.502	0.614	1.502
1.50	0.525	0.652	2.025

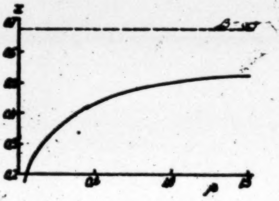


Fig. 4

Increase in the coefficient β is associated with rise in relative vapor pressure p/p_s. The magnitude x represents the relative distance of the middle of the meniscus from the point of contact of the spheres. The values given in Table 1 hence indicate how the meniscus moves in accordance with increase in vapor pressure. Fig. 4 shows the relation between x and β, according to the values of Table 1, and also gives the limiting position of the meniscus, corresponding to the broken line for $p/p_s = 1$, derived as above. We see that for small β (small p/p_s) the distance x between the middle of the meniscus and the point of contact of the spheres rises rapidly, and that the rate of increase is strongly retarded as p/p_s approaches unity. The relationship found is independent of the size of the spheres and of physical constants, i.e., the curve of Fig. 4 is a universal one.

4. Volume of condensed liquid in a sorption cell, for the general case.

The volume of condensed liquid in sorption cells for different values of β or p/p_s can be calculated from the values of the parameters of the meridianal curve found above. It is obvious that this volume may be represented as the difference between two volumes:

$$v = V_N - 2w.$$

The first of these, V_N is the volume of the figure of rotation (nodoid) given by rotation of an arc of a trochoid around the z axis, limited by planes of origin parallel to the r axis. The second volume 2w is that of segments of the spheres, tangential to the nodoid.

The volume V_N is derived as the volume of a figure of rotation, using formula (17):

$$V_N = 2\pi \int_0^{z_0} r^2 dz = 2\pi \int_{r_1}^{r_0} \frac{r_1 r_2 r^2 - r^4}{\sqrt{(r_2^2 - r^2)(r^2 - r_1^2)}} dr. \qquad (30)$$

Here r_0 and z_0 are the coordinates of the point of contact. Introducing the previous symbols from (19), (19^I), and (19^{II}), we substitute for the variable in formula (30), to obtain:

$$V_N = 2\pi r_2^2 \int_{\phi_0}^{\pi/2} [r_1 \cdot \Delta\phi - r_2 (\Delta\phi)^2] d\phi$$

or

$$V_N = 2\pi r_1 r_2^2 \int_{\phi_0}^{\pi/2} \Delta\phi \cdot d\phi - 2\pi r_2^3 \int_{\phi_0}^{\pi/2} (\Delta\phi)^2 d\phi. \qquad (31)$$

The first of these integrals is an elliptic integral of the first order, and the second may be reduced to a combination of elliptic integrals. It can be shown that [7]

$$\int_0^{\phi} (\Delta\phi)^2 d\phi = {}^2/_3 \frac{r_1^2 + r_2^2}{r_2^2} \int_0^{\phi} \Delta\phi d\phi - {}^1/_3 \frac{r_1^2}{r_2^2} \int_0^{\phi} \frac{d\phi}{\Delta\phi} + \frac{r_2^2 - r_1^2}{6 r_2^2} \sin 2\phi \cdot \Delta\phi. \qquad (32)$$

Substituting the expression (32) into formula (31), and taking into account the integration limits, we obtain:

$$V_N = {}^2/_3\,\pi\left\{r_1^2 r_2\ \Phi(\alpha,\ \phi_0) + {}^1/_2\,r_0\,(r_2^2 - r_1^2)\sin 2\,\phi_0 - [2(r_2 - r_1)^2 + r_1 r_2]r_2\ \Psi(\ \alpha,\ \phi_0)\right\} \qquad (33)$$

Here $\Phi(\alpha,\ \phi_0)$ and $\Psi(\alpha,\ \phi_0)$ are differential elliptic integrals for the argument ϕ_0, in accordance with formulation (20^1).

The doubled volume 2w of the spherical segment is given by

$$2w = {}^1/_3\,\pi z_0\,(3r_0^2 + z_0^2). \qquad (34)$$

The previous non-dimensional parameters x, β, and x_0 are introduced into formulas (33) and (34), when the volume v of condensed vapor can be represented as

$$v = {}^2/_3\,\pi R^3 \cdot U, \qquad (35)$$

where the non-dimensional function U has the form

$$U = (2 + x_0^2)\sqrt{1 - x_0^2} + x^2(x + \beta)\cdot\Phi(\alpha,\ \phi_0) + {}^1/_2\,x_0\,\beta(\beta + 2x)\sin 2\,\phi_0 - [2\beta^2 + x(x + \beta)]\,(x + \beta)\,\Psi(\alpha,\ \phi_0) - 2. \qquad (36)$$

TABLE 2

β	U	β	U
0.05	$1.43\cdot10^{-3}$	0.50	$32.49\cdot10^{-3}$
0.10	$3.44\cdot10^{-3}$	0.60	$39.45\cdot10^{-3}$
0.20	$9.90\cdot10^{-3}$	0.80	$53.84\cdot10^{-3}$
0.30	$17.45\cdot10^{-3}$	1.00	$70.66\cdot10^{-3}$
0.40	$24.67\cdot10^{-3}$	∞	$209.4\cdot10^{-3}$

The values of the parameters x and x_0, entering into expression (36), are found for different given values of β by the method described above. The corresponding values of α and ϕ_0 are derived from formulas (28) and (29). The integrals Φ and Ψ are found from the tables. For a given radius R of the sphere the relation (36) expresses the relative change in the volume of condensed vapor with change in β, i.e., with change in vapor pressure. Table 2 gives the calculating values of U for certain β, derived by means of formula (36). The values of U for various intermediate β are found from the graph drawn on the basis of the values of Table 2, not shown in this paper.

The last column of the Table gives the value of U for full saturation (when $p/p_s = 1$), derived by us above from the volume of the catenoid (formula 10) for the limiting case. The relative volume U is a universal function of β, independent of the radius of the sphere, and of physical constants. If we introduce the relative vapor pressure p/p_s, and express U as a function of this variable, it becomes evident that the value of U rises as that of R falls. Formula (35) allows us to calculate the volume v of condensed vapor at different p/p_s, and for spheres of different radii.

As an example, we have calculated U and v for spheres of different radii, for capillary condensation of benzene at 20°; the following constants were taken: σ = 28.9 ergs/sq. cm.; d_{20} = 0.879 g/cm^3.; M = 78.11. Since $C = \dfrac{2\sigma V}{2.3R_0T}\cdot(\log p_s/p)^{-1}$, we obtain the following, after substituting the values of the physical constants:

$$C = 0.917\cdot10^{-7}\cdot(\log p_s/p)^{-1}.$$

TABLE 3

p/p_s	$R = 1\cdot10^{-6}$ cm		$R = 5\cdot10^{-6}$ cm		$R = 1\cdot10^{-5}$ cm		$R = 5\cdot10^{-5}$ cm	
	U%	$v\cdot10^{-2}\ m\mu^3$	U%	$v\cdot10^{-2}\ m\mu^3$	U%	$v\cdot10^{-8}\ m\mu^3$	U %	$v\cdot10^{-2}\ m\mu^3$
0.50	1.77	0.371	0.16	4.2	0.07	14.7	0.01	262
0.60	2.58	0.541	0.26	6.8	0.10	21.0	0.015	393
0.80	6.57	1.377	0.92	24.1	0.32	67.0	0.04	1049
0.90	12.4	2.60	2.48	65	0.99	207	0.095	2490
0.95	16.7	3.50	5.57	146	2.57	540	0.26	6820
1.00	20.9	4.39	20.9	550	20.9	4390	20.9	$55\cdot10^4$

Table 3 gives the values of U and v for spheres of different radii, and for certain relative pressures p/p_s. The values of $\beta = C/R$ are calculated using the above value for the parameter C.

The results given in the Table point to certain features of the sorption system under consideration, due to its geometrical properties. The magnitude U is, as is evident from formula (35), a quarter of the relative volume of capillary-condensed liquid, i.e., it shows what fraction of the volume of the sorption cell is occupied by the liquid in it. It is evident from the data of Table 3 that this fraction is in general a small one, not exceeding about 5% at its limiting value. It is further evident that it falls steeply as the radius of the sphere increases. On the other hand, the volume of sorbed liquid rises steeply as the size of the spheres increases. Finally, the calculation shows that with increase in vapor pressure the volume $\underline{v}$ rises, at first gradually, and then quite steeply, especially for large particles.

When we proceed to the analysis of the process in systems formed of large numbers of spheres we shall see how these properties of sorption cells affect the total magnitude of sorption, and what effect they have on the form of the capillary condensation isotherms.

The author has pleasure in acknowledging his gratitude to M. M. Dubinin for the interest he has taken in this research, and to A. V. Kiselev and V. V. Serpinsky for their useful advice.

SUMMARY

1. A theoretical analysis of the process of capillary condensation in a system consisting of two contiguous spherical particles of the same radius has been conducted.

2. An expression has been found for the meniscus of the liquid in a sorption cell, on the assumption of full wetting, and the volume of sorbed vapor has been calculated as a function of the vapor pressure.

3. The behavior of a sorption cell has been shown to follow from its geometrical properties.

Received April 15, 1952

Institute of Physical Chemistry
Academy of Sciences USSR

LITERATURE CITED

[1] R. Zsigmondy, Z. anorg. Chem. 71, 356 (1911); J. McGavack, Jr. and W. A. Patrick, J. Am. Chem. Soc. 42, 946 (1920); P. Kubelka, Z. Elektrochem. 37, 367, (1931); P. Kubelka, Kolloid Z. 55, 129 (1931); ibid, 58, 189 (1932); G. Lindau, Kolloid Z. 60, 253 (1932); L. H. Cohan and G. E. Meyer, J. Am. Chem. Soc. 62, 2715 (1940).

[2] J. L. Shereshefsky, J. Am. Chem. Soc. 50, 2966 (1928); ibid. 50, 2980 (1928); J. L. Shereshefsky and C. P. Carter, J. Am. Chem. Soc. 72, 3682 (1950).

[3] K. V. Chmutov. Sorption phenomena in capillary systems (Thesis, All-Union Academy of Chemical Defence), Moscow, 1940; K. V. Chmutov. Colloid. J. , 10, 47 (1948); 11, 44 (1949).

[4] T. Schoon and H. W. Koch, Kautschuk 17, 1 (1941); O. Heering, V. Gizye and K. J. Kirsek, Kautschuk 17, 56 (1941); A. Ragoss, U. Hofmann and R. Holst, Kolloid Z. 105, 118 (1943); P. H. Emmett and T. De Witt, Ind. Eng. Chem. (Anal. Ed) 13,28 (1941); R. B. Anderson and P. H. Emmett, J. Appl. Phys. 19, 367 (1948); C. E. Hall, J. Appl. Phys. 18, 588 (1947); ibid. 19, 271 (1948); J. H. L. Watson, J. Appl. Phys. 20, 747 (1949); S.S. Voyutsky and S. I. Rubina. Prog. Chem. 21, 84 (1952).

[5] A. Winkelmann, Handb. d. Phys. 1,2 H., cited by F. Pockels, Kapillaritat, S. 1149. Leipzig, 1908.

[6] E. Jahncke and F. Emde. Tables of functions with formulas and curves. 2nd Ed. GITTL, Moscow 1949.

[7] I. M. Ryzhik. Tables of integrals, sums of series, and derivatives. 2nd Ed. OGIZ, Moscow 1948, p. 96, No. 23.

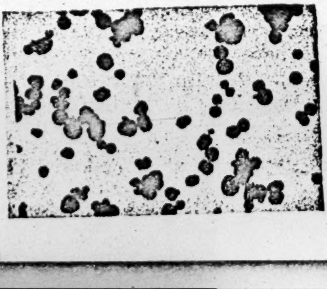


Fig. 1.

CATALYTIC OXIDATION OF PHOSPHINE OVER A WIDE RANGE OF TEMPERATURES

E. A. Andreev and N. N. Kavtaradze

INTRODUCTION

We have in our earlier papers [1,2] given a detailed description of the results of research on the catalytic oxidation of phosphine at moderate temperatures (18-120°), in presence of charcoal activated with copper salts. We found that, together with a rapid process of physical adsorption, a specific irreversible process of adsorption of phosphine by copper oxides took place. The kinetics of the combined (physical and irreversible) adsorption of phosphine is expressed by a parabolic equation [3]

$$q = At^{1/n},$$

where q is the amount of adsorbed gas, A is a constant, t is time, and $1/n$ is an index of the degree.

We showed that the catalytic oxidation of phosphine on charcoal treated with copper salts involves a stage of chemisorption on copper oxide on charcoal. The kinetics of oxidation of phosphine in the adsorption layer may, over the range 18-120°, be represented by the Roginsky-Zeldovich equation [4]:

$$\log(t + t_0) = \frac{\alpha}{1.3} q - \log (\alpha a),$$

where a is the initial velocity, α is a constant, q is the amount of adsorbed gas, $t = 1/\alpha a$, and t is time in minutes. We thought it would be of interest to investigate this same reaction at higher temperatures.

Before proceeding to describe the results of our studies of the catalytic oxidation of phosphine over the range 264-320°, we shall briefly review published views on the state of the surface of active charcoal. Such a surface, in contact with damp air, adsorbs molecules of water, carbon dioxide, and oxygen. Shilov and Chmutov [5] suppose that in addition to physically adsorbed molecules of oxygen there may exist, under different conditions, three surface oxides, having different ratios of carbon to oxygen.

At 320°, and in a vacuum given by a mercury-diffusional pump, we achieve not only total elimination of physically adsorbed oxygen, but also partial desorption of the oxygen chemically bound by the surface of the charcoal as oxides of carbon. Chemisorbed oxygen is tenaciously retained by the surface of active charcoal, since the heat of adsorption of oxygen at low saturations is close to that of formation of oxides of carbon [6,7]. Complete removal of chemisorbed oxygen from the surface of active charcoal is not achieved even at 900°, with prolonged evacuation.

EXPERIMENTAL

Experimental methods, and preparation of samples of charcoal with chemisorptive and catalytic properties

The apparatus described in our preceding paper, with quartz spring balances, was used for the study of catalytic oxidation of phosphine at 200-320°. The accuracy of the measurements was in most cases within 0.1% by weight, and the temperatures varied by ± 0.5°. The experiments on adsorption and desorption were conducted according to the methods described in our earlier paper [2]. As in our previous researches, we used as the carrier for the catalytic additives ground recuperational carbon AP, with a grain diameter of 1.5 to 2.5 mm., and an ash content of 8%. The specific surface of this charcoal, as determined by the methylene blue method, amount to 410 sq.m/g.

The processes of adsorption and desorption of methanol were studied, in order to obtain a fuller picture of the behavior of the recuperational carbon as an adsorbent.

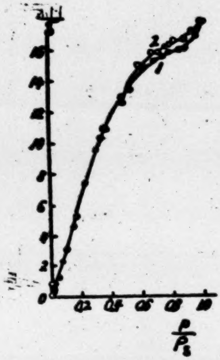


Fig. 1. 1) Adsorption isotherm, 2) desorption isotherm for methanol, at 20°, for recuperational carbon, subjected to preliminary training in high vacuum at 400°.

Fig. 1 is based on measurements made in A. V. Kiselev's laboratory, and shows the adsorption (1) and desorption (2) isotherms for methanol at 20°, on recuperational carbon previously trained at 400° in high vacuum. The radii of the capillaries were calculated from the Thomson formula, for the desorption branch of the isotherm

$$r = \frac{2\sigma V \cos\theta}{RT\, 2.3 \log p_s/p}$$

In this formula the surface tension of liquid methanol $\sigma = 22.55$ erg/sq. cm., the gas constant $\underline{R} = 8.315 \times 10^7$ erg/°/mol., the relative pressure of methanol being designated as p/p_s, where p_s is the saturated vapor pressure of the adsorbate at the experimental temperature.

The process of desorption can, as was shown by Zhdanov [8], be described by the above formula, irrespective of whether the pores end blindly or pass right through the granules. The results of the calculations suggest that the pores of our charcoal are largely of the transitional type.

One sample of charcoal with additives, designated AP-1, was prepared by impregnating a weighed sample of AP charcoal with a solution of copper sulfate, so as to give a product containing 4% of copper, after drying. A second sample, designated AP-2, was prepared in the same way, but was treated with aqueous ammonia before drying, and was then heated at 250-300° for 3-6 hours; in this sample the cuprammonium salts underwent decomposition when heated, yielding oxides of copper.

We shall show that water is quite tenaciously retained by the oxides of copper. According to Fricke and Hüttig [9] the process of dehydration of dry cupric oxide monohydrate in a stream of dry air proceeds through a series of stages, each with a different water content.

Adsorption and chemisorption of phosphine by recuperational carbon with and without additives

The experiments on adsorption of phosphine were conducted at high temperatures, under conditions excluding the possibility of contamination of the adsorbent by lubricant or mercury vapors. With this object, the training of the adsorbent at 315° and the adsorption of phosphine were conducted with the use of carbon dioxide snow as a coolant, at -78°, both in the Dewar vessel attached at the quartz spring-balance and in that with the U-tube. The most interesting feature of the experiments at sufficiently high temperatures was the oxidation of adsorbed phosphine by oxygen, which was irreversibly adsorbed and chemically bound by both the active charcoal and the copper additive.

a) Chemisorption of phosphine by recuperational carbon without additives, and desorption of the products of surface reaction

We first had to determine to what extent oxygen actively adsorbed or chemically bound by the surface of the adsorbent takes part in the process of chemisorption of phosphine. Special experiments with 100 mg portions of active charcoal were undertaken with this object, at 315°, first measuring the kinetics of adsorption of phosphine (Curge 1, Fig. 2) at 110 mm, and then desorbing (Curve 2, Fig. 2) by means of a portion of degassed active charcoal contained in a vessel cooled in liquid air.

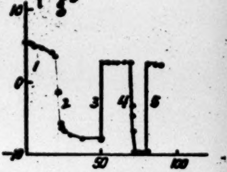


Fig. 2. 1) Adsorption of phosphine at 315°/110 mm by active charcoal, without additives; 2) desorption at 315°; 3) repeated adsorption at 315°/102 mm; 4) desorption at 315°; 5) repeated adsorption of phosphine at 315°/102 mm.

The amount of desorbed product was three times greater than was the amount of adsorbed phosphine, showing that it was a product of reaction of phosphine with oxygen actively adsorbed on the surface of the charcoal. Repeated adsorption of phosphine (Curve 3, Fig. 2) gave very little oxidation, because most of the oxygen had been used up in the first adsorption-desorption cycle. The amount of phosphine adsorbed in the second cycle was considerably greater than in the first, probably because phosphine molecules occupy places on the adsorbent surface previously occupied by oxygen molecules. In the third cycle the amount of desorbed phosphine is exactly equal to that adsorbed, showing that it was recovered unchanged.

b) Chemisorption of recuperational carbon with copper salt additives and desorption of products of the surface reaction.

High temperature adsorption of phosphine on charcoals with copper additives, and subsequent desorption, proceed quantitatively differently to the case of adsorbent without additives. Fig. 3 shows that total (physical and chemisorption) adsorption of phosphine falls as the temperature rises from 130 to 264° (Curves 1 and 2, Fig. 3), above which it rises with temperature (Curve 4, Fig. 3). These effects are explained by supposing that although physical adsorption falls, specific adsorption (chemisorption) rises with increase in temperature to 320°.

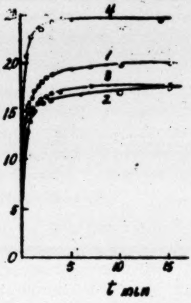


Fig. 3. Adsorption of phosphine on active charcoal AP-2, containing copper additives: 1) at 130°/102 mm; 2) at 264°/102 mm; 3) at 264°/105 mm; 4) at 320°/102 mm.

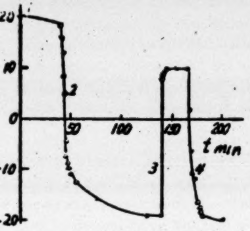


Fig. 4. 1) Adsorption of phosphine at 320°/102 mm on active charcoal AP-2; 2) desorption; 3) repeated adsorption of phosphine at 320°/102 mm; 4) repeated desorption.

The Table gives values for adsorption of phosphine, in mg/g, and also for desorption of phosphine and its oxidation products. The same Table also gives results for the amount of adsorbed oxygen, in mg/g, after desorption of phosphine and its oxidation products.

At 264° and 320° the desorption process proceeds differently, according to the experimental conditions, judging from the amount of desorbed product, as well as from the amount of oxygen remaining in adsorption (see Table).

It was of interest to ascertain whether the oxygen of adsorbent AP-2 is all used up after the first chemisorption of phosphine at p = 100 mm, for which reason special experiments involving repeated adsorption of phosphine were performed. Curve 1 of Fig. 4 represents the process of adsorption of phosphine at 320° on a fresh portion of adsorbent AP-2. Curve 2 represents the process of desorption of the products of chemisorption of phosphine, Curve 3 the process of repeated adsorption of phosphine on the same adsorbent, and Curve 4 the process of repeated desorption. As in the absence of additives, considerably enhanced adsorption (45 % more) of phosphine was found in the second adsorption-desorption cycle.

This finding supports the view that the parts of the surface which were in the fresh adsorbent occupied by oxygen molecules were, on repeating adsorption, occupied by phosphine molecules. Thus during primary adsorption of phosphine the first stage of the reaction involves formation of a phosphine-oxygen compound.

TABLE

Temperature, °C	Adsorption of phosphine, mg/g	Desorbed phosphine and its oxidation products, mg/g	Adsorbed oxygen, mg/g	Remarks
320	25	47.5	52.5	Desorbed by means of active charcoal cooled to the temperature of liquid nitrogen.
264	21.4	20.8	53.2	
264	21.4	2.0	22.9	Exhausted by means of a mercury-diffusional pump.

The weight of products desorbed after the second adsorption only slightly exceeds (by 7%) the amount of phosphine adsorbed, showing that nearly all the available oxygen was used up in the chemisorption reaction of the first cycle.

Adsorption of oxygen by active charcoal treated with phosphine at high temperatures

We have shown earlier [1, 2] that raising the temperature of degassing from 17 to 320° leads to an increase in the amount of chemisorbed phosphine from 5.3 to 9.2 ml/g NTP. Experiments on oxidation of chemisorbed phosphine by gaseous oxygen at 17° showed that a considerable part of the phosphine in chemisorption on charcoal previously evacuated at 320° does not undergo oxidation at 17°. Thus, phosphine adsorbed on special parts of the adsorbent surface, which are made accessible only by training at high temperature, does not react with gaseous oxygen at 17°.

We shall show that the process of adsorption of phosphine proceeds identically on specimens of adsorbent with added copper sulfate, with or without subsequent treatment with ammonia. The process of adsorption of oxygen is much more rapid on adsorbents treated with ammonia and heated after addition of copper sulfate (Curve 2, Fig. 5), so that their copper is in the form of oxide, than in the case of adsorbents treated with copper sulfate alone. Thus the process of oxidation is greatly accelerated at room temperature on charcoals containing oxides of copper, as compared with those containing sulfate.

The magnitude and the velocity of adsorption of oxygen at 264-320° on charcoal containing copper compounds, and on which phosphine had first been adsorbed and then desorbed, depend very largely on the conditions of desorption. Desorption by means of charcoal cooled in liquid nitrogen leads to elimination of a considerable part of the products of chemisorption of phosphine. Thus at 320° the weight of desorbed product is twice as great as the weight of adsorbed phosphine. An abrupt rise in the velocity and amount of adsorption of gaseous oxygen is observed, as compared with charcoal which had been subjected to desorption effected by means of a mercury-diffusional pump.

The five curves of Fig. 6 represent the kinetics of adsorption of oxygen at ~ 9.5 mm, at different temperatures. It is evident that Curves 4 and 5, at 320°, differ relatively little from Curve 3, which represents adsorption kinetics at 264°. In all these experiments portions of charcoal AP-2 were first treated with phosphine at a pressure p = 105 mm. The method used for desorption of the products of the surface reaction was the same in all cases, viz., exposure to charcoal cooled in liquid nitrogen. The final values for adsorption of oxygen were practically identical in experiments 3, 4, and 5, amounting to q = 52.5 mg/g at 320°, and 53.4 mg/g at 264°, irrespective of the large differences in the values for preliminary desorption.

The kinetics of adsorption of oxygen at 264° were very different (Curve 2, Fig. 6) when the products of the surface reaction of phosphine with actively adsorbed oxygen were desorbed by means of evacuation with a mercury-diffusional pump. Adsorption of any contaminants (mercury or tap-grease vapors) was excluded by means of double or triple traps cooled in liquid air.

Adsorption of oxygen on charcoal AP-2 in the experiments represented by Curves 5, 4 and 3, Fig. 6 is equal to the amount of oxygen needed for total oxidation of the adsorbed phosphine. The experimental results indicate that at 264-320° actively adsorbed phosphine is oxidized largely by oxygen which is actively adsorbed and chemically bound both by the carbon and by the copper additive. We shall call this the surface reaction of oxidation of phosphine.

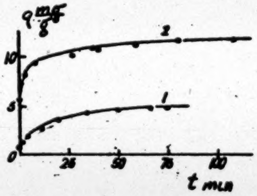


Fig. 5. Adsorption of oxygen: 1) adsorption of oxygen at 19°/10 mm on active charcoal with added copper sulfate, without subsequent treatment with ammonia, and containing 9 mg/g of irreversibly adsorbed phosphine; 2) adsorption of oxygen at at 17.5°/9.5 mm by active charcoal AP-2 (treated with ammonia), containing 9.6 mg/g of irreversibly adsorbed phosphine.

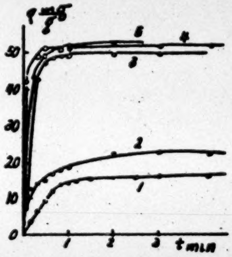


Fig. 6. Adsorption of oxygen at 320° by portions of active charcoal AP-2 on which phosphine had previously been adsorbed and desorbed: 1) at 130°/9 mm; 2) at 264°/10.5 mm; 3) at 264°/9 mm; 4) at 320°/9 mm; 5) at 320°/9.5 mm.

The identical results for adsorption of oxygen on activated charcoal at 264 and 320° may perhaps be due to the previously desorbed product being fully oxidized (P_2O_5; H_2O), since subsequent adsorption of oxygen is unaffected by the presence of this substance.

It may be thought that after partial desportion of the product of chemosorption of phosphine, in total absence of oxygen and at 264-320° it should be possible to obtain a carbon and a metal surface free of actively adsorbed or chemically bound oxygen. Formation of a metal surface free of oxygen is, according to

Roginsky [10], possible only in exceptional cases, at the very end of the catalytic process in presence of excess of oxidized substance.

A confirmation of the hypothesis of formation of a surface of high activity with respect to oxygen during the process of stepwise adsorption of phosphine and desorption of the products of its chemisorption at 264-320° is afforded by the following observation. After desorption at 264° of the product of chemisorption of phosphine the surface of the charcoal AP-2 combines rapidly with considerable amounts of oxygen at pressures of the order of 10^{-4} mm. An increase in weight due to adsorption is observed when the quartz spring-balance is connected with mercury-diffusional and oil vacuum pumps, even when it is protected from access of mercury and oil vapors by three traps cooled in liquid air (Curve 3, Fig. 7).

The kinetics of adsorption of phosphine are shown by Curve 1, Fig. 7, and desorption of the products of chemisorption of phosphine is represented by Curve 2, and adsorption of oxygen at 264°/9 mm by Curve 4. A rough calculation shows that under these conditions (264°/10^{-4} mm) only a few collisions of oxygen molecules from the gaseous phase are needed for them to become adsorbed.

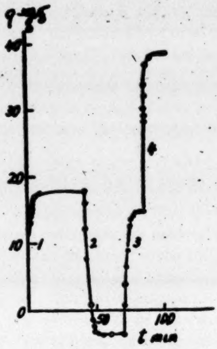


Fig. 7. Adsorption of phosphine on activated charcoal AP-2 at 264°/105 mm; 2) desorption of products of surface reaction of phosphine with adsorbed oxygen; 3) adsorption of oxygen at 264°/10^{-4} mm; 4) adsorption of oxygen at 264°/10.5 mm.

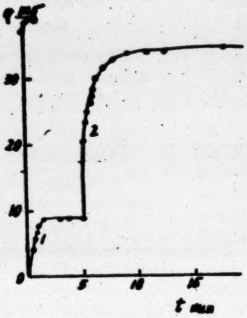


Fig. 8. 1) Adsorption of oxygen at 264°/0.015 mm; 2) adsorption of oxygen at 264°/ 10 mm.

A special experiment was performed with a portion of charcoal AP -2 on which phosphine had first been adsorbed at p = 75 mm and 264°, and the products of surface oxidation of phosphine were then desorbed. Curve 1, Fig. 8, represents kinetics of adsorption of oxygen at 264°/0.015 mm, and Curve 2 represents kinetics of adsorption of oxygen at p = 10 mm.

In connection with the above Bruns' paper [11] on activated adsorption of oxygen by active charcoal, and its role in the catalytic process, is of interest. This author found that only those molecules of oxygen which were loosely bound to the active charcoal displayed catalytic activity, while strongly bound oxygen was unreactive. In our opinion this may be true for the catalytic oxidation of phosphine at room temperature, but at 264-320° practically all of the oxygen, both adsorbed and chemically bound to charcoal AP-2, is used up in the chemisorption of phosphine.

Repeated cycles of stepwise oxidation of phosphine on charcoal containing copper compound additives

Experiments on adsorption and desorption of phosphine on charcoal AP -2 with subsequent adsorption (chemisorption of oxygen from the gaseous phase is of considerable interest, from the point of view of regeneration of active centers of catalysts. Our experiments were conducted at 264 and 320°; Fig. 9 represents two repeated cycles at 320°.

The first cycle of stepwise oxidation is represented by Curve 1, which shows adsorption of phosphine at p = 102 mm; Curve 2 represents desorption of products of surface oxidation of phosphine; Curve 3 relates to adsorption of oxygen from the gaseous phase (left-hand branch of Curve 3) and desorption (right-hand branch of Curve 3) before the second cycle. A characteristic feature of this cycle is that maximum desorption of the substance takes place after the surface reaction of phosphine with the oxygen bound to the catalyst.

The second cycle of stepwise oxidation includes the same processes; chemisorption of phosphine (in spite of the slightly lower pressure than in the first cycle) is represented by Curve 4, and is somewhat greater than in the first cycle.

It is evident that formation of catalyst took place during the first cycle, and was followed by desorption of the product of the surface reaction of phosphine with catalyst oxygen (Curve 5, Fig. 9), and finally by adsorption of oxygen, represented by Curve 6, Fig. 9, which was found to be equal to that found in the first cycle.

The stepwise catalytic process of oxidation of phosphine may thus be regarded as one of alternating reduction and oxidation of the catalyst surface.

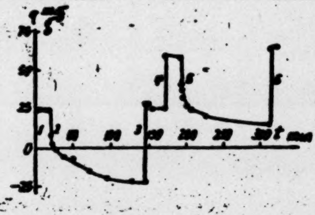


Fig. 9. Repeated cycles of stepwise oxidation of phosphine at 320°, on charcoal AP-2: 1) adsorption of phosphine at 102 mm; 2) desorption; 3) adsorption of oxygen at 9 mm; 4) repeated adsorption of phosphine at 88 mm; 5) desorption; 6) adsorption of oxygen at 88 mm.

Preliminary experiments on chemisorption of phosphine on cuprous and cupric oxide

Experimental study of the role of the carrier of additives catalyzing the reaction of oxidation of phosphine showed that the nature of the surface and the porosity of the carrier play a quite important part in formation of the catalysts. The active charcoal is not only the carrier of the catalytic additive; as we have shown above there is no doubt that chemisorption and subsequent oxidation of phosphine take place at its surface at elevated temperatures. At 18° the process of irreversible specific adsorption takes place only on highly dispersed copper compounds on charcoal. In contradistinction to charcoal AP-2 finely powdered commercial granular cupric and cuprous oxides only weakly adsorb phosphine (~ 2 mg/g) at room temperature. This may be ascribed in the first place to the much smaller specific surface of these oxides than when they are on the carrier, and in the second place to the activity of these oxides being much lower than when they are on charcoal.

As the temperature rises to 130° adsorption of phosphine on both cuprous and cupric oxide rises sharply, attaining 9-10 % of the weight of the catalysts when these were previously treated with oxygen at 130°/30 mm for 20-30 min. The results obtained for kinetics of adsorption of phosphine by cuprous and cupric oxide at 130°/100 mm are shown by the curves of Fig. 10. Adsorption of phosphine on cupric oxide (Curve 2) proceeds much more slowly than for cuprous oxide, under the same conditions, and, in addition, there is an induction period of about 10 minutes during which no adsorption takes place. This is followed by a fairly steep rise in velocity of adsorption, so that the reaction between cupric oxide and phosphine may be regarded as a topochemical process.

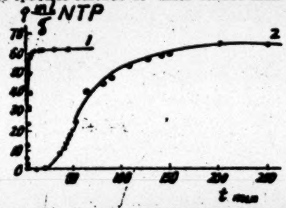


Fig. 10. Adsorption of phosphine by oxides of copper at 130°/100 mm: 1) adsorption of phosphine by cuprous oxide; 2) adsorption of phosphine by cupric oxide.

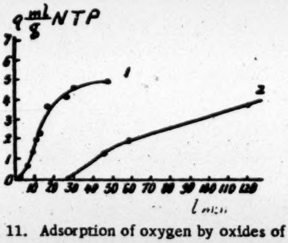


Fig. 11. Adsorption of oxygen by oxides of copper containing chemisorbed phosphine, at 130°: 1) adsorption of oxygen by cuprous oxide at 30 mm; 2) adsorption of oxygen by cupric oxide at 34 mm pressure.

Curve 1, Fig. 10, represents the kinetics of adsorption of phosphine by cuprous oxide. The process begins as soon as the phosphine is introduced, and it proceeds with uniform speed practically until achievement of equilibrium. After completion of adsorption of phosphine and of desorption (7.1 mg/g were desorbed) we subjected the irreversibly adsorbed phosphine to oxidation. Adsorption of oxygen at 130°/30 mm (Curve 2, Fig. 11) by cupric oxide previously treated with phosphine proceeded more slowly than with cuprous oxide (Curve 1, Fig. 11) also previously treated with phosphine.

The velocity of oxidation of chemisorbed phosphine on cupric oxide is much smaller than on Charcoal AP-2 with copper compound additive. This can be ascribed in the first place to the greater specific surface of copper compounds when adsorbed on charcoal, and in the second to the specific action of charcoal as a component of the compound catalyst.

Catalytic oxidation of phosphine in mixtures with oxygen in static conditions

Experiments on catalytic oxidation of phosphine mixed with oxygen were conducted at pressures, p = 0.4 mm or less, because at higher pressures spontaneous ignition of mixtures of the stoichiometric composition $PH_3 + 2O_2$ took place. We used a quartz spring balance for the study of oxidation kinetics for phosphine-oxygen mixtures in the presence of charcoal AP-2 with copper salt, at 18°, at which temperature the oxidation products are retained by the catalyst. In order to minimize pressure changes during experiments of greater duration the $PH_3 + 2O_2$ mixture was prepared in a 6-liter flask. The kinetics of the process are illustrated by the curve of Fig. 12.

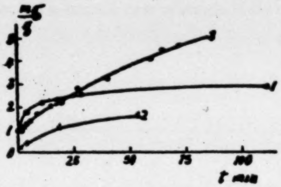


Fig. 12. 1) Adsorption of phosphine at 18.3°/0.1 mm; 2) adsorption of oxygen at 18.3°/27 mm; 3) oxidation of phosphine in $PH_3 + 2O_2$ mixture at 21°/0.4 mm.

It is evident that for pressures of about 0.4 mm of the phosphine-oxygen mixture, and at 18°, the activated adsorption process is not a stage limiting the velocity of oxidation of phosphine. Under these circumstances such a stage is that of oxidation of already chemisorbed molecules of phosphine. Calculation of the velocity constants of the reaction of catalytic oxidation from first and second order equations gave values falling steeply and regularly with time; after 60 minutes they were only a tenth of their initial values. This may be ascribed firstly to the non-homogeneity of the catalyst surface, and secondly to retardation of the reaction due to non-volatile oxidation products.

DISCUSSION OF RESULTS

The experimental results allow us to draw certain conclusions, and to advance a reaction scheme for oxidation of phosphine catalyzed by charcoal with copper salt additives, at 18-320°.

The fastest reaction is that of physical adsorption of phosphine. Simultaneously with physical adsorption we have specific irreversible sorption of phosphine, the rate of which increases with rise in temperature. There is no doubt that catalytic oxidation of phosphine takes place through the stage of specific adsorption. We have shown that presence of specific chemical adsorption is an essential although not a sufficient, condition for the catalytic oxidation of phosphine. Catalytic oxidation of phosphine molecules in chemisorption on copper sulfate (at 20°) proceeds only very feebly, as is also the case for the process (at 20°) at particular locations of active charcoal with oxides of copper, rendered vacant by training at high temperatures in vacuo. It may, from our experiments, be concluded that it is the cuprous form of the copper compound present in the catalysts which is responsible for initiating the reaction of oxidation of phosphine.

At high temperatures chemisorption of phosphine takes place not only on the copper additive, but also at the charcoal surface, which may be regarded under these circumstances as a catalyst of oxidation of phosphine. A complex of phosphine and oxygen formed at the surface undergoes surface oxidation at the expense of oxygen combined with the charcoal surface. The products of surface oxidation may be desorbed as oxides of phosphorus and water, and the adsorbent-additive surface thus liberated possesses considerable reactivity with regard to fixation of gaseous molecular oxygen. The amount of phosphine in chemisorption of the surface of recuperational charcoal itself, at 320°, was only 20% of the amount found with charcoal containing copper salts.

It is of interest to compare the number of molecules of chemisorbed phosphine with the number of copper atoms per gram of catalyst. Active charcoal AP-2 contains 4% of copper, i.e., 40 mg/g, or 3.9 x 10^{20} atoms of copper. The maximum amount of phosphine in chemisorption at 320° is 24.7 mg/g, of which 5.7 mg is bound by the surface of the charcoal itself. The copper additive has thus been responsible for chemisorption of 19 mg, or 3.39 x 10^{-20} molecules of phosphine. It follows that at 320° each atom of copper present as oxide binds not more than one molecule of phosphine.

It may be concluded from all the available data that the primary specific adsorption of the phosphine molecule involves the participation of the oxygen present on the surface of the charcoal, and its additive, and that subsequent reactions with gaseous oxygen lead to completion of the reaction of oxidation of phosphine, and to the regeneration of the catalyst surface. The catalytic process of oxidation of phosphine should be regarded as a succession of oxidation and reduction processes following rapidly one after the other; at room temperature transfer of oxygen is due to oxides of copper. At elevated temperatures the process of successive oxidations and reductions takes place not only at the additive surface, but also at the surface of the charcoal itself, which acquires a chemisorbed oxygen layer.

Chemisorption of phosphine at the charcoal surface at elevated temperatures should be regarded as a reaction of reduction by phosphine of superficial oxide of carbon.

The oxidation products (oxides, not acids) may be desorbed from the catalyst by exposure to charcoal cooled at the temperature of liquid air. Chemisorption of phosphine by copper salt additives may be represented for the particular case of cupric oxide on charcoal by the following schemes:

$$PH_3 + CuO = H_3PO + Cu; \qquad (1)$$

$$2Cu + O_2 = 2CuO; \qquad (2)$$

$$H_3PO + CuO = Cu + H_3PO_2; \qquad (3)$$

$$H_3PO_2 + CuO = Cu + H_3PO_3; \qquad (4)$$

$$H_3PO_3 + CuO = Cu + H_3PO_4; \qquad (5)$$

$$4H_3PO_2 = 2PH_3 + P_2O_5 + 3H_2O; \qquad (6)$$

$$3H_3PO_3 = H_3PO + P_2O_5 + 3H_2O \qquad (7)$$

It is possible that in addition to these reactions part of the phosphine reacts with copper compounds at elevated temperatures to give copper phosphide as an intermediate product; we were able, however, only in a few cases to detect formation of very small amounts of copper phosphide.

SUMMARY

1. Presence of specific chemical adsorption of phosphine on active charcoal with additives is an essential, although not a sufficient, condition for initiation of the process of catalytic oxidation of phosphine.

2. On catalytic charcoal the most firmly chemisorbed molecules of phosphine are only very slowly oxidized by oxygen at room temperature.

3. The cuprous form of copper appears to be responsible for initiation of catalytic oxidation of phosphine.

4. At elevated temperatures the surface of the charcoal itself, without additives, acts catalytically in oxidation of phosphine by atmospheric oxygen.

5. In absence of atmospheric oxygen, and at elevated temperatures, phosphine reacts with oxygen bound to the catalyst AP-2, to give oxides of phosphorus and water. Desorption of these products leaves a surface which adsorbs gaseous oxygen with exceptional avidity.

6. The first stage of chemisorption of phosphine is the formation of a phosphine-oxygen complex at the catalyst surface.

7. The process of catalytic oxidation of phosphine by gaseous oxygen at the surface of active charcoal containing copper oxides involves formation of intermediate compounds, with very rapidly alternating stages of reduction and oxidation of the catalyst. The catalyst is copper oxides at room temperature, while at elevated temperatures the charcoal surface itself can act as a catalyst, without additives.

LITERATURE CITED

[1] E. A. Andreev and N. N. Kavtaradze. Proc. Acad. Sci. 60, 1193 (1948).

[2] E. A. Andreev and N. N. Kavtaradze. Problems of kinetics and catalysis. 6, 293, U.S.S.R. Acad. Sci. Press (1949).

[3] Bangham, Phil. Mag. 5, 373 (1928).

[4] S. Z. Roginsky and Ya. B. Zeldovich, Acta. Phys. Chim. U.S.S.R. 1, 554 (1934).

[5] N. A. Shilov, E. Shatunovskaya, and K. V. Chmutov, Z. Phys. Chem. 150, p. 31, (1930).

[6] Lendle, Z. Phys. Chem. 172, 77 (1935).

[7] Garner, J. Chem. Soc. 49, 156 (1927).

[8] S. P. Zhdanov. Proc. Acad. Sci. USSR, 61, 853 (1948).

[9] R. Fricke nd G. Hüttig, Hydroxyde und Oxylhydrate, 1938.

[10] S. Z. Roginsky. Problems of kinetics and catalysis. 4, 181 (1940).

[11] B. P. Bruns. J. Phys. Chem. 21, No. 9 (1947).

Received May 26, 1952

Institute of Physical Chemistry
Academy of Sciences, U.S.S.R.

ELECTRON ABSORPTION SPECTRA OF POLYSTYRENE AND ITS DERIVATIVES

M. V. Volkenshtein and N. S. Kolodina

The study of the electron spectra of polymers is of fundamental importance, for both theoretical and practical reasons. It would, on the one hand, be of interest to find new spectrum analytical evidence throwing light on the composition and structure of polymers. On the other hand, it would be of interest to elucidate the effect of regularities in the structure of chain polymers on the electron spectrum. As the experimental work of Obreimov, Prikhotko, Rodnikova, and Eichis [1] has shown, the reaction of regularly distributed molecules in crystals leads to significant differences between the spectra of these crystals and of the molecules of which they are composed.

The theory of spectra of molecular crystals was advanced by Davidov [2], who showed that resonance reactions of molecules in crystals, which may be regarded as spreading of the exciting waves (excitons), should lead to the appearance of new, highly polarized lines in the electron spectrum. It might be thought that the same sort of phenomenon is possible also in linear polymers.

EXPERIMENTAL

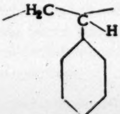
The polymers taken for study were those which had characteristic absorption in the sufficiently close ultra-violet region of the spectrum. We investigated polystyrene and the polymers of some halogen derivatives of styrene, comparing the spectra of the polymers with those of the hydrogenated monomers, taking the spectra under strictly comparable conditions – in solutions in the same solvents, and at the same molar concentrations, calculated on the basis of the monomer unit. The following pairs were studied:

1. Polystyrene – ethylbenzene ;
2. Poly-o-bromostyrene – o-bromotoluene ;
3. Poly-2,5-dichlorostyrene – 2,5-dichloroethylbenzene .

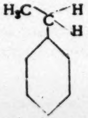
All spectra were in chloroform solution, the concentration for the first pair being 0.019 M (calculated for ethylbenzene), and of the same order for the other two pairs. The absorption spectrum of polystyrene in cyclohexane did not differ significantly from that in chloroform. The quartz spectrograph ISP-22 and the quartz photoelectric spectrophotometer SF-11 were used for our study. In the first case quartz cells were taken, the thickness of the layer varying from 0.05 to 10 mm.

Fig. 1 shows the absorption curves for polystyrene and ethylbenzene in chloroform, obtained by the usual methods of photographic photometry. The same Fig. 1 gives the absorption curve for styrene in chloroform. The styrene spectrum differs considerably from those of polystyrene and ethylbenzene, which is a natural consequence of the differences in the chemical structure of these substances.

The spectra of polystyrene and ethylbenzene are practically identical. This is evidence that the spectrum of polystyrene in the given region is determined by electron transfers located in the individual units of the molecule or, more exactly, in the benzene ring:



Polystyrene unit



Ethylbenzene

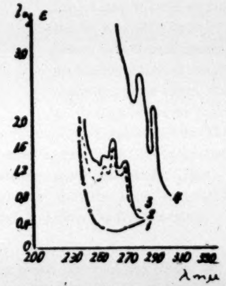
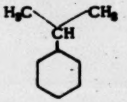


Fig. 1. 1) Chloroform; 2) polystyrene in chloroform; 3) ethylbenzene in chloroform; 4) styrene in chloroform.

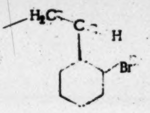
Small differences between the spectra of polystyrene and ethylbenzene may be connected with differences in their structure. An even better coincidence between the spectra of polystyrene and isopropylbenzene might be expected:



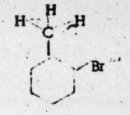
Oscillatory structure is well expressed in the spectrum, the positions of the maxima of the absorption bands being at 269, 262, 255, and 249 mμ. The distances between the maxima correspond to the frequency of vibration of the benzene molecule. Thus, in this case polymerization has no effect on the spectrum in the region of the benzene ring absorption bands. "Collective" spectrum bands, similar to those seen in the spectra of molecular crystals, are not observed in the spectrum of polystyrene. This is evidence that the polystyrene chain is not regularly distributed in space; the polymer is similar to a fluid, but not to a crystal.

The considerable differences between the electron absorption spectra of polystyrene and styrene make it possible to apply a spectrophotometric method to the determination of unpolymerized styrene and polystyrene in their mixtures.

Fig. 2 gives the absorption curves of polybromostyrene and o-bromotoluene in chloroform:

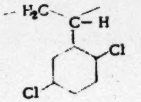


Polymer unit

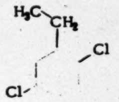


o-Bromotoluene

The results obtained are similar to those obtained for polystyrene. The spectra of the polymer and the monomer are practically identical. The positions of the absorption maxima (vibratory structure) for the polymer are at 278, 269, 262, and 255 mμ. Fig. 3 gives the absorption curves of poly-2,5-dichlorostyrene and 2,5-dichloroethylbenzene in chloroform:



Polymer unit



2,5-Dichloroethylbenzene

The result obtained for this case was more interesting. Here also the spectra of the monomer and the polymer are practically identical, but the polymer spectrum is shifted by 30 A from the spectrum of the monomer. The absorption maxima of the polymer spectrum are at 284, 276, 269 and 261 mμ.

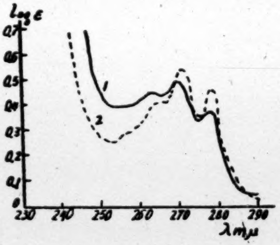


Fig. 2. 1) Poly-o-bromostyrene; 2) o-Bromotoluene.

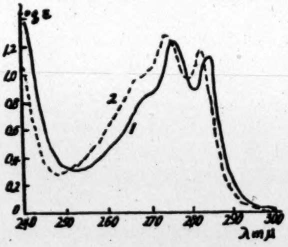
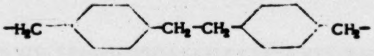


Fig. 3. 1) Poly-2,5-dichlorostyrene; 2) 2,5-dichloroethylbenzene.

The available data do not permit the formulation of any simple explanation of this shift in the spectrum. It may perhaps be due to resonant reaction of the benzene rings, similar to that found in molecular crystals. The regularity in their distribution may be due to interaction of symetrically disposed dipoles C–Cl. On the other hand, it is possible that the observed shift of the spectrum of the polymer in the direction of greater wave-lengths is determined by ordinary Van der Waals' forces acting within one and the same molecule. The determining factor would again be the dipole moment of the C–Cl bond, and we suppose that the latter assumption is the more probable one. In any case, polymerization here gives rise to a perceptible effect on the electron absorption spectrum.

Experiments performed at low temperatures would be needed for a more profound study of the effect of polymerization on the electron absorption spectrum. Since the results obtained by us give evidence of the noncrystalline nature of the polymers it is not to be expected that the low temperature spectra would manifest any specific effects, such as are found in the spectra of molecular crystals. It might nevertheless be thought that the low-temperature spectra of the polymers would more clearly reveal the oscillatory structure of the bands.

We also investigated the spectrum of polyphenylenethyl[*]:



Polyphenylenethyl, which may be regarded as an isomer of polystyrene, is a dark brown, viscous, resinous substance. It was not found possible, using any of the known chemical methods, to eliminate colored impurities from it. The spectroscopic study should, in particular, have revealed whether the coloration was due to presence of impurities, or to the substance itself. The latter supposition is contradicted by all that is known of the coloration of organic compounds.

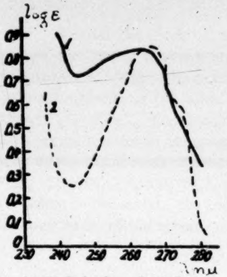
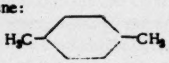


Fig. 4. 1) Polyphenylenethyl; 2) p-Xylene.

Fig. 4 shows the absorption curves of chloroform solutions of polyphenylenethyl and p-xylene:



p-Xylene can be regarded as an analog of the individual unit of the polyphenylenethyl chain. We see that the spectra of the polymer and the monomer resemble each other very closely, both having the same intense absorption band at 264 mμ. Polyphenylenethyl has no very clear-cut absorption bands in the long wave region. We suppose that the similarity between the spectra of polyphenylenethyl and p-xylene is evidence that the coloration of the polymer was due to the presence of small amounts of tarry matter formed during polymerization.

We have pleasure in expressing our gratitude to Docent L. V. Smirnov for his help.

SUMMARY

1. A comparison has been made of the ultraviolet absorption spectra of polystyrene and of certain of its derivatives with the spectra of substances having a structure analogous to that of the monomer units of the polymers.

2. Resemblances and differences in the spectra of the polymers and the analogs of their monomer units have been established. The spectrum of polyphenylenethyl is found to resemble that of p-xylene.

LITERATURE CITED

[1] A. F. Prikhotko. Bull. U.S.S.R. Acad. Sci., Physical Series 12, 499 (1948); A. Yu. Eichis. ibid. 14 (1950).

[2] A. S. Davidov. Theory of absorption of light in molecular crystals. Ukrainian S.S.R. Acad. Sci. Press. Kiev (1951).

Received May 18, 1952

Institute of High-Molecular Compounds
Academy of Sciences, U.S.S.R.

---

[*] We take pleasure in thanking V. V. Korshak for supplying us with a specimen of this substance.

BLANK
PAGE

PREPARATION OF TRICHLOROALKOXYTITANES FROM TITANIUM TETRACHLORIDE AND ALCOHOLS

A. N. Nesmeyanov, R. Kh. Freidlina, and O. V. Nogina

Friedel and Crafts [1] showed in 1870 that titanium tetrachloride and diethyl ether gave a crystalline product, distillation of which afforded ethyl chloride, diethyl ether, and a second crystalline product, the composition of which corresponded, according to these authors, to the formula $C_2H_5OTiCl_3$. The reaction was again examined later [2], when two double salts were isolated, of the composition $C_2H_5OC_2H_5 \cdot TiCl_4$ and $3C_2H_5OC_2H_5 \cdot 2TiCl_4$, thermal decomposition of which gave trichloroethoxytitane. A further paper was published [3] in which a series of compounds of titanium tetrachloride with esters were described. The author obtained three double compounds of ethyl acetate with titanium tetrachloride, of the compositions $2TiCl_4 \cdot CH_3COOC_2H_5$; $TiCl_4 \cdot CH_3COOC_2H_5$ and $TiCl_4 \cdot 2CH_3COOC_2H_5$, and analogous compounds were obtained with ethyl benzoate. According to the author, the compounds obtained were complex compounds of trichloroethoxytitane and dichlorodiethoxytitane, of the types:

$$2TiCl_4 \cdot CH_3COOC_2H_5 = C_2H_5OTiCl_3 \cdot TiCl_4 \cdot CH_3COCl;$$

$$TiCl_4 \cdot CH_3COOC_2H_5 = C_2H_5OTiCl_3 \cdot CH_3COCl;$$

$$TiCl_4 \cdot 2CH_3COOC_2H_5 = (C_2H_5O)_2TiCl_2 \cdot 2CH_3COCl.$$

This author based his views on the fact that trichloroethoxytitane obtained by him, apparently by the Friedel-Crafts method, gave the same compound with titanium tetrachloride and acetyl chloride as was obtained from an equimolecular mixture of titanium tetrachloride and ethyl acetate.

It seems to us to be unlikely that formation of trichloroethoxytitane, which requires fairly drastic reaction conditions, could result from the mere mixing of the reagents. More probably, double compounds of titanium tetrachloride with esters are produced in these conditions. As for the reaction of trichloroethoxytitane with acetyl chloride, this may proceed as follows:

$$C_2H_5OTiCl_3 + CH_3COCl \longrightarrow TiCl_4 \cdot CH_3COOC_2H_5.$$

A fairly recent paper [4] mentions an attempt at preparation of trichloroethoxytitane, apparently by the reaction of dichlorodiethoxytitane with acetyl chloride, but the expected product was not obtained.

We thus see that only one of the trichloroalkoxytitanes, viz., trichloroethoxytitane, has up till now been prepared [2]. The reaction whereby it was prepared is a complex one, giving rise to a number of by-products, and suffers from the disadvantage that many ethers (such as ethers of sec.- and tert-alkyls) are not readily available.

Luchinsky [5], in studying the reaction of titanium tetrachloride with phenols, found that phenol and m-nitrophenol gave trichloroaryloxytitanes, whereas p-chlorophenol and o- and p-nitrophenol gave dichlorodiaryloxytitanes. This author did not investigate why certain phenols replaced only one chlorine atom, whereas others replaced two.

As part of our study of aliphatic derivatives of titanium [6,7,8] we decided to work out a method of synthesis of trichloroalkoxytitanes from titanium tetrachloride and alcohols. All the published work on the direct action of alcohols on titanium tetrachloride has been done under conditions of large excess of alcohol [4], and the sole products were the double compounds of dichlorodialkoxytitanes with alcohols, $(RO)_2TiCl_2 \cdot ROH$. Since it was obvious that this reaction must have passed through the stage of trichloroalkoxytitane, we thought that if it were to be conducted with excess of titanium tetrachloride it should give trichloroalkoxytitanes as the main product.

This was found to be the case: the sole product obtained by heating ethanol with a ten-fold excess of titanium tetrachloride was trichloroethoxytitane. We found that the reaction was more conveniently conducted when inert solvents were added, when only a relatively small excess of titanium tetrachloride needs to be taken. The solvents tried were carbon tetrachloride and light petroleum. It is essential that the solution of the alcohol should be added to titanium tetrachloride, and not vice versa. After mixing the solutions the systems were boiled for several hours, until evolution of hydrogen chloride was complete, the solvent was distilled off, and the residue was fractionally distilled under reduced pressure.

This method for the synthesis of trichloroalkoxytitanes is convenient and simple, and gives quantitative yields of products. The method was tried with primary n- and isoalcohols, and with alcohols with substituents in the chain.

The products obtained were trichloro-ethoxytitane, -n-propoxytitane, -isobutoxytitane, -isoamyloxytitane, and -n-hexoxytitane, which are crystalline, hygroscopic, readily hydrolyzable substances. They have low melting points, and can be distilled in vacuum without decomposition. They are readily soluble in diethyl ether and benzene, and more sparingly soluble in carbon tetrachloride, light petroleum, or chloroform.

Trichloro-β-methoxyethoxytitane, $CH_3OCH_2CH_2OTiCl_3$ differs from the above products in having a much higher m.p., and in its insolubility in ordinary solvents.

EXPERIMENTAL

All the reactions were conducted with scrupulously dried reagents, and under conditions such that access of atmospheric moisture was excluded.

Preparation of trichloro-n-propoxytitane (n-$C_3H_7OTiCl_3$). A solution of 30 g (0.5 mole) of thoroughly dried n-propanol in 200 ml of light petroleum was added from a dropping funnel to a solution of 142.5 g (0.75 mole) of titanium tetrachloride in 300 ml of light petroleum (fraction boiling at 50-80°) in a flask fitted with a phosphorus pentoxide tube. Vigorous evolution of hydrogen chloride proceeded for about an hour, after which the solution was boiled on the water bath. Part of the solvent was then distilled off, and the residue was cooled in a freezing mixture. The precipitate formed was distilled at 11 mm, boiling at 83-85°; when redistilled the b.p. was 100-102° at 23 mm. The yield of crude product was 103 g (96.5%).

	Found %:	C 16.79; 16.79;	H 3.19; 3.38;	Cl 49.64; 49.65;	Ti 22.10; 22.16
$C_3H_7OTiCl_3$.	Calculated %:	C 16.88;	H 3.31;	Cl 49.86;	Ti 22.45.

Trichloro-n-propoxytitane is a light yellow, crystalline substance, m.p. 65-67° (sealed capillary). It is hygroscopic, and is readily hydrolyzed.

Preparation of trichloroethoxytitane $C_2H_5OTiCl_3$. The procedure was as above. A solution of 23 g (0.5 mole) of absolute ethanol in 200 ml of light petroleum (b.p. 50-80°) was added gradually to 142 g (0.75 mole) of titanium tetrachloride in 300 ml of light petroleum, and the mixture was boiled on the water bath for 8 hrs until evolution of hydrogen chloride had ceased. The mixture was left until the next morning, when the supernatant liquid was decanted off from the precipitate which had formed, and most of the solvent was distilled off from it. The residue was cooled in freezing mixture, when a further portion of precipitate separated from it, giving a total yield of 87 g (87.5%). The light yellow, crystalline product was hygroscopic, and was readily hydrolyzable. It boiled at 185-186°/760 mm; the published value of the b.p. of $C_2H_5OTiCl_3$ [2] is 186-188°.

	Found %:	C 12.09; 11.85;	H 2.38; 2.47;	Cl 53.21; 53.27;	Ti 23.90; 23.62
$C_2H_5OTiCl_3$.	Calculated %:	C 12.04;	H 2.53;	Cl 53.37;	Ti 24.03.

Preparation of trichloroisobutoxytitane iso-$C_4H_9OTiCl_3$. The procedure was as before, except that carbon tetrachloride was taken as the solvent. A solution of 24.7 g (0.33 mole) of isobutanol in 100 ml of carbon tetrachloride was added gradually to 95 g (0.5 mole) of titanium tetrachloride in 125 ml of carbon tetrachloride, and the mixture was boiled for 9 hours. The crystalline product separating from the cooled solution boiled at 92-94° at 9 mm, and the m.p. of the distilled product (sealed capillary) was 81-83°.

	Found %:	C 21.39; 21.72;	H 3.81; 4.17;	Cl 46.42; 45.73;	Ti 21.14, 20.82
$C_4H_9OTiCl_3$.	Calculated %:	C 21.13;	H 3.99;	Cl 46.78;	Ti 21.06.

The yield of crude product was practically theoretical. Trichloroisobutoxytitane is a hygroscopic crystalline substance, readily hydrolyzable.

Preparation of trichloroisoamyloxytitane iso-$C_5H_{11}OTiCl_3$. The same procedure was applied as before. A solution of 44 g (0.5 mole) of isoamyl alcohol in 200 ml of light petroleum was added to 142.5 g (0.75 mole) of titanium tetrachloride in 300 ml of light petroleum, and the mixture was boiled for 5 hrs on the water bath, until evolution of hydrogen chloride ceased. The cooled solution gave 115 g of product (95.5% of theory). The light yellow crystalline product is hygroscopic and readily hydrolyzable; it boils at 110-111°/17 mm, and the distilled substance melts at 50-60° (sealed capillary).

Found %: C 24.91; 24.63; H 4.88; 4.95; Ti 19.52; 19.56
$C_5H_{11}OTiCl_3$. Calculated %: C 24.87; H 4.59; Ti 19.84.

Preparation of trichloro-n-hexoxytitane n-$C_6H_{13}OTiCl_3$. The procedure was as above. A solution of 40 g (0.39 mole) of n-hexanol in 150 ml of light petroleum was added gradually to 112 g (0.58 mole) of titanium tetrachloride in 150 ml of light petroleum. A precipitate formed as soon as the reagents were mixed. The mixture was boiled for 3 hrs, until evolution of hydrogen chloride had ceased.

Trichloro-n-hexoxytitane is a light yellow crystalline substance, and is hygroscopic and readily hydrolyzable. It boils at 120-122°/8 mm, and the m.p. of the twice-distilled product is 47.5-49° (sealed capillary). The yield is practically quantitative.

Found %: Cl 40.86; 41.33; Ti 18.70; 18.90
$C_6H_{13}OTiCl_3$. Calculated %: Cl 41.65; Ti 18.75.

Preparation of trichloro-β-methoxyethoxytitane $CH_3OCH_2CH_2OTiCl_3$. The method was the same as before. A solution of 38 g (0.5 mole) of β-methoxyethanol in 125 ml of carbon tetrachloride was added gradually to 142.5 g (0.75 mole) of titanium tetrachloride in 150 ml of carbon tetrachloride, and the mixture was boiled for 4 hrs. The precipitate separating was collected; it is insoluble in light petroleum, carbon tetrachloride, benzene, or diethyl ether. It was analyzed after repeated washing with light petroleum (30-50°) and diethyl ether, and drying in vacuum.

Found %: C 15.80; 15.84; H 3.16; 3.22; Cl 46.33; 46.40; Ti 20.50; 20.40
$CH_3OCH_2CH_2OTiCl_3$. Calculated %: C 15.71; H 3.08; Cl 46.38; Ti 20.88

The product slowly distills over when heated on an oil bath, at 160-180°/5 mm, and the distilled substance melts at 164-166° (sealed capillary). The yield of crude product is close to the theoretical.

SUMMARY

1. A new method for the synthesis of trichloroalkoxytitanes, based on the reaction of alcohols with titanium tetrachloride, is described.

2. The following new products were obtained: trichloro-n-propoxytitane, -isobutoxytitane, -isoamyloxytitane, -n-hexoxytitane, and -β-methoxyethoxytitane.

Received May 29, 1952

Institute of Organic Chemistry
Academy of Sciences USSR

LITERATURE CITED

[1] M. Friedel, M. Crafts, Bull. Soc. Chim. (2), 14, 98 (1870).

[2] P. P. Bedson, J. Chem. Soc., 29, 309 (1876).

[3] E. Demarcay, Bull. Soc. Chim. (N.S.), 20, 127 (1873).

[4] J. S. Jennings, W. Wardlaw, W. J. R. Way, J. Chem. Soc., 637 (1936).

[5] G. P. Luchinsky, J. Gen. Chem., 6, 481 (1936); 7, 2045 (1937).

[6] O. V. Nogina, R. Kh. Freidlina, and A. N. Nesmeyanov, Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 3, 327 (1950).

[7] A. N. Nesmeyanov, R. Kh. Freidlina, and O. V. Nogina. Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 5, 518 (1951).

[8] O. V. Nogina, R. Kh. Freidlina, and A. N. Nesmeyanov, Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 1, 76 (1952). (See Consultants Bureau English Translation, p. 81.)

BLANK
PAGE

SYNTHESIS OF AROMATIC ARSENIC-ORGANIC COMPOUNDS THROUGH ARYLAZOCARBOXYLIC SALTS

O. A. Reutov and Yu. G. Bundel

Nesmeyanov [1] and Ptitsina and one of us [2] have elaborated a method of synthesis of aromatic compounds of mercury and antimony, by the reaction of potassium arylazocarboxylates with mercuric chloride or antimony trichloride, as follows:

$$ArN_2CO_2K + HgCl_2 \longrightarrow ArHgCl + N_2 + CO_2 + KCl; \; ArN_2CO_2K + SbCl_3 \longrightarrow ArSbCl_2 + N_2 + CO_2 + KCl.$$

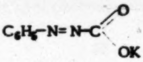
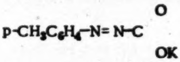
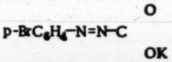
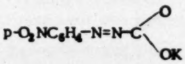
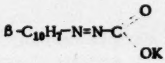
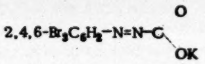
This method has in the present paper been extended to the synthesis of arsenic-organic compounds.

As was expected, arylazocarboxylic salts readily reacted with cold solutions of arsenic trichloride in acetone or ethyl acetate, giving the appropriate arsenic-organic compounds, from potassium phenylazo-, p-tolylazo-, p-bromophenylazo-, p-nitrophenylazo-, β-naphthylazo-, and 2,4,6-tribromophenylazo-carboxylate.

A detailed study of the reaction between potassium phenylazocarboxylate and arsenic trichloride showed that the optimum conditions were gradual addition of the salt to acetone solution of arsenic trichloride (50% excess) at room temperature, with constant stirring. The same conditions were applied to all the arylazocarboxylates with arsenic trichloride.

Separation of the arsenic-organic compounds formed was effected after their alkaline hydrolysis * into the corresponding arylarsine oxides or arylarsenious acids. The results are given in the Table.

Reaction of arylazocarboxylic acid salts with arsenic trichloride
Reaction temperature 18-20°; solvent-acetone; excess of $AsCl_3$ 50%

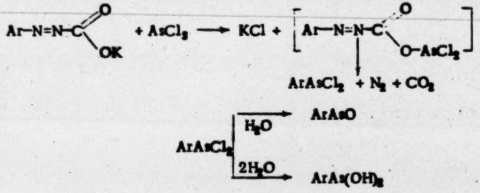
Serial No.	Arylazocarboxylic acid salt	Reaction products, %			Total yield, %
		ArAsO	$(Ar_2As)_2O$	$ArAs(OH)_2$	
1	 $C_6H_5-N=N-C(=O)OK$	42	21	–	63
2	 $p\text{-}CH_3C_6H_4-N=N-C(=O)OK$	32	20	–	52
3	 $p\text{-}BrC_6H_4-N=N-C(=O)OK$	47	34	–	81
4	 $p\text{-}O_2NC_6H_4-N=N-C(=O)OK$	–	–	64	64
5	 $\beta\text{-}C_{10}H_7-N=N-C(=O)OK$	–	–	30	30
6	 $2,4,6\text{-}Br_3C_6H_2-N=N-C(=O)OK$	36	–	–	36

As is evident from the Table, the reaction products are monoarylarsine oxides, diarylarsine oxides, and monoarylarsenious acids, i.e., exclusively tervalent arsenic derivatives; this differs from the results for the synthesis of antimony-organic compounds through arylazocarboxylic salts [2], where both ter- and quinque-valent antimony derivatives are formed.

Formation of monoarylarsine oxides, arylarsenious acids, and diarylarsine oxides appears to proceed according to the following schemes:

---

* 2,4,6-Tribromophenyldichloroarsine was hydrolyzed by water without addition of alkali.



$$2Ar{-}N{=}N{-}COOK + AsCl_3 \longrightarrow Ar_2AsCl^{*} + 2N_2 + 2CO_2 + 2KCl$$

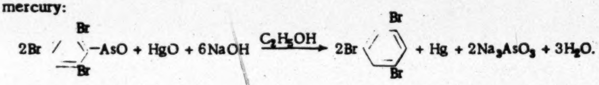
$$2Ar_2AsCl \xrightarrow{H_2O} (Ar_2As)_2O$$

It is of interest that 2,4,6-tribromophenyldichloroarsine is given by the reaction between potassium 2,4,6-tribromophenylazocarboxylate and arsenic trichloride, since attempts at preparing analogous mercury-organic [1] and antimony-organic [2] compounds were unsuccessful. It seems that tribromophenyl compounds of mercury or antimony cannot be formed, owing to steric hindrance of the two bromine atoms in the ortho-position. Owing to the smaller size of the As atom (the Van der Waals radii of Hg, Sb, and As atoms are respectively 2.3, 2.2, and 2.0 A) steric hindrance is much smaller, or even entirely absent; moreover, an important factor connected with formation of the tribromophenyl derivative of arsenic is the high stability of the arsenic-carbon link, in general.

Although aromatic arsenic-organic compounds generally yield mercury-organic compounds [3] when treated with mercuric oxide in alkaline media, according to the equation

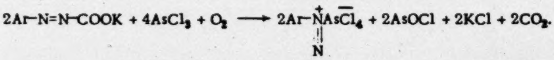
$$2\,ArAsO + HgO + 6NaOH \longrightarrow Ar_2Hg + 2Na_3AsO_3 + 3H_2O,$$

2,4,6-tribromophenylarsine oxide reacts differently under these conditions, forming 1,3,5-tribromobenzene and metallic mercury:



We found that the addition of zinc dust to the reaction mixture obtained from potassium phenylazocarboxylate or p-bromophenylazocarboxylate and $AsCl_3$ gives vigorous evolution of nitrogen. This is evidence that the products of reaction between arylazocarboxylates and $AsCl_3$ include not only arsenic-organic compounds, but also double salts of aryldiazonium chloride with arsenic trichloride.**

Formation of ArN_2Cl, $AsCl_3$, as also formation of Mey salts in the reaction between ArN_2CO_2K and $SbCl_3$ [3], proceeds with participation of atmospheric oxygen, as follows:



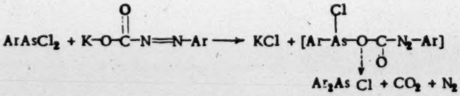
$$2Ar{-}N{=}N{-}COOK + 4AsCl_3 + O_2 \longrightarrow 2Ar{-}\underset{\underset{N}{\|}}{\overset{+}{N}}\overline{AsCl_4} + 2AsOCl + 2KCl + 2CO_2.$$

This reaction proceeds much more readily than does the analogous reaction with $SbCl_3$; the zinc dust test shows the presence of the double diazonium salt in the reaction mixture immediately after addition of ArN_2CO_2K to the $AsCl_3$ solution, whereas in the case of $SbCl_3$ contact of the reaction solution with atmospheric oxygen for several hours is necessary. If the reaction between ArN_2CO_2K and $AsCl_3$ is conducted in a stream of nitrogen, so as to exclude access of atmospheric oxygen, the double diazonium salt is not formed.

We were not able to isolate $ArN_2Cl \cdot AsCl_3$ in a pure state from the reaction mixture by the same method as was applied to isolation of Mey's salts in the reaction between arylazocarboxylates and antimony trichloride [2].

---

* It is possible that diarylchloroarsine is formed by the reaction between aryldichloroarsine and potassium arylazocarboxylate:



$$ArAsCl_2 + K{-}O{-}\overset{\overset{O}{\|}}{C}{-}N{=}N{-}Ar \longrightarrow KCl + [Ar{-}\overset{\overset{Cl}{|}}{As}{-}O{-}\underset{\underset{O}{\|}}{C}{-}N_2{-}Ar] \downarrow Ar_2AsCl + CO_2 + N_2$$

** Salts of arylazocarboxylic acids are not decomposed by zinc dust.

This result was not, however, unexpected, since the double salts of p-tolyldiazonium chloride and $AsCl_3$ described in the literature ($C_7H_7N_2Cl \cdot AsCl_3$ and $C_7H_7N_2Cl \cdot 2AsCl_3$) are very unstable [4]. In order to study the properties of the double salt of phenyldiazonium chloride and $AsCl_3$ we prepared this compound in acetone solution by the reaction:

$$C_6H_5N_2Cl \cdot FeCl_3 + AsCl_3 \longrightarrow C_6H_5N_2Cl \cdot AsCl_3{}^{*} + FeCl_3,$$

precipitating the $C_6H_5N_2Cl \cdot AsCl_3$ from solution by addition of ether. The solid product can be stored for several hours without decomposition, but it decomposes very quickly in acetone or ethyl acetate solution, and in particular in contact with ether.**

We were able to demonstrate the formation of the double salt of $C_6H_5N_2Cl$ and $AsCl_3$ in the reaction between $C_6H_5N_2CO_2K$ and $AsCl_3$ in the following way. The reaction between potassium phenylazocarboxylate and arsenic trichloride was conducted at low temperature in toluene solution***, passing a stream of air. The precipitate formed, consisting of KCl, AsOCl, and $C_6H_5N_2Cl \cdot AsCl_3$, was collected by filtration, and was washed with small portions of acetone. The double salt of phenyldiazonium chloride and arsenic trichloride, which is dissolved out by the acetone, was converted by the action of mercuric chloride into the much more stable salt of phenyldiazonium chloride and mercuric chloride, which served for identification:

$$C_6H_5N_2Cl \cdot AsCl_3 + HgCl_2 \longrightarrow C_6H_5N_2Cl \cdot HgCl_2 + AsCl_3.$$

EXPERIMENTAL

1. Reaction of potassium phenylazocarboxylate with arsenic trichloride. 7 g of potassium phenylazocarboxylate (for preparation see [5] and [6]) was added during 10 min. to a solution of 10.2 g of arsenic trichloride (50 % excess) in 150 ml of dry acetone at room temperature, with stirring, which was continued for a further 20 min. The inorganic precipitate which separates (4.1 g) was collected and washed with small portions of acetone. The solvent was evaporated off from the filtrate**** under reduced pressure, at 35-40°. The residual brown mass was twice washed with cold 1:1 hydrochloric acid (30 and 15 ml) and with water (15 ml), and was then heated at 90-100° with 15 ml of 40% KOH in a porcelain basin. The hot mixture was filtered through a glass filter, on which a residue of 0.8 g of diphenylarsine oxide, contaminated with tarry matter, remained; it melted at 86-88° after recrystallization from light petroleum.

Cooling the filtrate in freezing mixture gave a precipitate consisting of potassium chloride and diphenylarsine oxide, from which KCl was eliminated by washing with water, leaving 0.15 g of diphenylarsine oxide, the combined yield of which was thus 0.95 g (21% of theory); the m.p. was 88-90°, published m.p. 91-92° [7].

Addition of saturated ammonium chloride solution to the filtrate gave a precipitate of 2.6 g (42% of theory) of phenylarsine oxide, which was purified by repeated dissolution in chloroform and precipitation with ether. The m.p. was 127-130°; published values for the m.p. 119-121° [7] and 142-144° [8].

Found %: C 42.65; 42.75; H 2.80; 3.04
C_6H_5AsO. Calculated %: C 42.87; H 3.00

Found %: As 45.15
C_6H_5AsO. Calculated %: As 44.61

The combined yield of arsenic-organic compounds amounted to 63% of the theoretical.

---

* In reality an approximately equimolecular mixture of $C_6H_5N_2Cl \cdot AsCl_3$ and $(C_6H_5N_2Cl)_2 \cdot AsCl_3$ is formed.

** It is very probable that $ArN_2Cl \cdot AsCl_3$ is formed not only in the reaction between $C_6H_5N_2CO_2K$ or $p\text{-}BrC_6H_4N_2CO_2K$ and $AsCl_3$, but also in all other cases; their not being shown by the zinc dust test may be due to their decomposition in the first stage of the reaction between ArN_2CO_2K and $AsCl_3$.

*** Toluene was chosen as the solvent because the double diazonium salt is insoluble in it, and separates out as a precipitate. A low temperature was taken in order to retard the reaction between $C_6H_5N_2CO_2K$ and $AsCl_3$, and hence to prolong the time of contact of the reaction mixture with atmospheric oxygen.

**** Addition of zinc dust to the filtrate gives energetic evolution of nitrogen.

2. Reaction of potassium p-tolylazocarboxylate with arsenic trichloride. 9.5 g of potassium p-tolylazocarboxylate (for preparation see [5]) was added during 10 min. to a solution of 12.5 g (50% excess) of arsenic trichloride in 200 ml of dry acetone at room temperature, with constant stirring, which was continued for a further 20 min. The inorganic precipitate (I) was collected and washed with small portions of acetone; it weighed 4.5 g. The solvent was removed from the filtrate by evaporation at 25-30° under reduced pressure, and the pasty brown residue was twice washed with cold 1:1 hydrochloric acid (30 and 15 ml), and was then added drop by drop to 30 ml of 50% KOH. The mixture solidified after a few minutes, when it was passed through a glass filter, giving precipitate (II), which was extracted on the filter with 80 ml of cold water. Addition to the extract of saturated aqueous NH_4Cl gave a precipitate of p-tolylarsine oxide, which was collected and washed with small portions of water; yield 2.2 g (32%). After washing with ether and recrystallizing from ethanol the product melted at 167-169°; published m.p. 156-158° [9].

Found %: C 46.30; 46.48; H 4.31; 4.33
C_7H_7AsO. Calculated %: C 46.19; H 3.88

Some di-p-tolylarsine oxide, contaminated with tarry matter, remained on the filter after treatment of precipitate (II) with water. Three recrystallizations from light petroleum gave 1.2 g (20% of theory) of product of m.p. 103-105°; published m.p. 98° [10].

Found %: C 63.12; H 5.50
$C_{28}H_{28}As_2O$. Calculated %: C 63.42; H 5.10.

The combined yield of arsenic-organic compounds was 3.4 g (52% of theory).

3. Reaction of potassium p-bromophenylazocarboxylate with arsenic trichloride. 4.5 g of potassium p-bromophenylazocarboxylate (for preparation see [11]) was added during 10 min. to a solution of 4.6 g of arsenic trichloride (50% excess) in 100 ml of dry acetone at room temperature, with constant stirring. The inorganic precipitate was collected (3.1 g) and washed with small portions of acetone. The solvent was removed from the filtrate[*] by evaporation at 25-30° under reduced pressure, and the residue was twice washed with cold 1:1 hydrochloric acid (25 and 10 ml), and then with water (10 ml), after which it was treated with 30 ml of 1:3 aqueous KOH. The mixture was filtered through glass, giving a residue of 1.0 g (34% of theory) of di-p-bromophenylarsine oxide, m.p. 157-159° after recrystallization from chloroform. The product, which has not previously been reported, is colorless, readily soluble in chloroform and acetone, moderately soluble in ethanol, and sparingly soluble in ether.

Found %: C 36.48; 36.34; H 2.39; 2.17
$C_{24}H_{16}OBr_4As_2$. Calculated %: C 36.49; H 2.04

Addition to the filtrate of 30 ml of saturated aqueous ammonium chloride gives 2.0 g (47% of theory) of p-bromophenylarsine oxide, m.p. 239-240°, after recrystallization from ethanol; published m.p. 259-261° [11].

Found %: C 29.13; 29.16; H 1.71; 1.88
BrC_6H_4AsO. Calculated %: C 29.18; H 1.63.

The combined yield of arsenic-organic compounds was 3.0 g (81% of theory).

4. Reaction of potassium p-nitrophenylazocarboxylate with arsenic trichloride. 8 g of potassium p-nitrophenylazocarboxylate (for preparation see [11]) was added during 10 min. to 9.3 g (50% excess) of arsenic trichloride in 150 ml of dry acetone at room temperature, with constant stirring. The inorganic precipitate (3.5 g) was collected and washed on the filter with small portions of acetone. The solvent was evaporated off from the filtrate at 25-30°, under reduced pressure, and the residue was twice washed with cold 1:1 hydrochloric acid, and then with water (15 ml) after which it was treated with 30 ml of 1:5 aqueous KOH. The solid hydrolysis product, which was p-nitrophenylarsenious acid, was collected and washed with water; yield 4.5 g (64% of theory). It was purified by repeated dissolution in concentrated aqueous KOH, and precipitation with hydrochloric acid, followed by thorough washing with ether. p-Nitrophenylarsenious acid is a light brown substance which decomposes explosively when heated; it is sparingly soluble in organic solvents. According to the literature [13] it is a brown substance, soluble in alkalis, exploding when heated.

---

[*] Addition of zinc dust to the filtrate causes vigorous evolution of nitrogen.

Found %: C 30.84; 30.75; H 2.43; 2.26
$O_2NC_6H_4As(OH)_2$. Calculated %: C 31.18; H 2.62

5. Reaction of potassium β-naphthylazocarboxylate with arsenic trichloride. 7.5 g of potassium β-naphthylazocarboxylate* was added during 10 min to a solution of 9 g of arsenic trichloride (50 % excess) in 150 ml of dry acetone at room temperature, with constant stirring. The inorganic precipitate separating (4 g) was collected and washed with acetone, and the solvent was evaporated off from the filtrate at 25-30° under reduced pressure. The residue was washed with cold 1:1 hydrochloric acid (50 and 25 ml) and with water (25 ml), and was then treated with dilute aqueous KOH (1:10) for 1 hr. As the β-naphthylarsenious acid so obtained is difficultly soluble in organic solvents it was purified by thorough washing with alcohol and ether; the m.p. was 140°. Yield 2.5 g (30%).

Found %: C 50.36; H 3.31
$C_{10}H_7As(OH)_2$. Calculated %: C 50.84; H 3.83

6. Reaction of potassium 2,4,6-tribromophenylazocarboxylate with arsenic trichloride. 3.7 g of potassium 2,4,6-tribromophenylazocarboxylate (for preparation see [14]) was added during 10 min to a solution of 4.7 g of arsenic trichloride (50% excess) in 125 ml of dry acetone at room temperature, with constant stirring. The inorganic precipitate separating (1.3 g) was collected and washed with acetone, and the solvent was evaporated off from the filtrate at 25-30° under reduced pressure. The residue solidified when cooled in a freezing mixture, and it was washed with 50 ml of 1:1 HCl and with water, collected on the filter, dried, and extracted with a large volume of ether. The residue after evaporation of the ether extract is tribromophenylarsine oxide, contaminated with tribromobenzene and tarry matter. 2,4,6-Tribromophenylarsine oxide was recrystallized from a large volume of ethanol, and was washed with ether; it is a colorless substance, difficultly soluble in the ordinary organic solvents, m.p. 219-220°, yield 1.55 g (36% of theory). It has not previously been described.

Found %: C 18.05; 17.98; H 0.56; 0.58; Br 59.39; 59.64
$C_6H_2OBr_3As$. Calculated %: C 17.78; H 0.50; Br 59.26

7. Preparation of the double salt of phenyldiazonium chloride and arsenic trichloride. 10 g of the double salt of phenyldiazonium chloride and ferric chloride (for preparation see [15]) was dissolved in the least volume of acetone, and 8 g of arsenic trichloride was added to the solution. The mixture was cooled in a freezing mixture, and ether was added until no further precipitate formed. The precipitate was collected and washed with cold acetone. It does not contain any $C_6H_5N_2Cl \cdot FeCl_3$ or $FeCl_3$ (tested with KCNS); it is readily soluble in water, sparingly soluble in acetone and ethyl acetate, and difficultly soluble in benzene and ether, although it readily decomposes when in contact with ether. It is unstable, marked decomposition being evident after 24 hrs. Its m.p. is 89-90° (decomposition).

Found %: N 10.81; 10.75

Analysis showed that the product is a mixture of two substances, $C_6H_5N_2Cl \cdot AsCl_3$ (calc. N content 8.70%) and $(C_6H_5N_2Cl)_2 \cdot AsCl_3$ (calc. N content 12.1%).

8. Reaction of 2,4,6-tribromophenylarsine oxide with mercuric oxide in alkaline media. A hot solution of 0.15 g of 2,4,6-tribromophenylarsine oxide in 1 ml of ethanol was added to a hot solution of 0.13 g of mercuric chloride in 1.5 ml of ethanol, followed by 0.75 ml of boiling aqueous 5 N sodium hydroxide, and the mixture was boiled for 2 min, and filtered off from the precipitate of metallic mercury. 7 ml of water was added to the cooled filtrate, and the precipitate (0.05 g) of 1,3,5-tribromobenzene, m.p. 118-120°, was collected; the published m.p. is 119-121° [16]. The product gave no m.p. depression with a specimen of tribromobenzene.

9. Conversion of the double salt of phenyldiazonium chloride and arsenic trichloride, formed in the reaction between $C_6H_5N_2CO_2K$ and $AsCl_3$, into a double salt of phenyldiazonium chloride and mercuric chloride. 8 g of potassium phenylazocarboxylate was added to a solution of 23 g (3-fold excess) of arsenic trichloride in toluene at -15°; evolution of gas was not observed. The temperature of the reaction mixture was raised during an hour to 20°, passing a stream of air through it (the reaction begins to proceed when the temperature of the mixture reaches 5°). The precipitate was collected after completion of the reaction; it consists of potassium chloride, arsenic oxychloride, and double salt of phenyldiazonium chloride and arsenic trichloride, and weighed 5.5 g. The precipitate was washed with benzene, and the double salt was extracted with 20 ml of acetone, when the residue weighed 3.5 g. A concentrated solution of 3 g of $HgCl_2$ in acetone was added to the acetone extract,

---

* Prepared by hydrolysis with alcoholic alkali of ethyl β-naphthylazocarboxylate.

followed by ether until no more white precipitate formed, and the double salt so obtained was twice reprecipitated from acetone with ether, to give a colorless substance, which gradually decomposes when heated at 100-130°. A suspension of the product in acetone or ethyl acetate is decomposed by addition of zinc dust. According to the literature [17] the double salt is a white, crystalline, infusible substance, which gradually decomposes when heated.

Found %: N 7.20; 7.02

$C_6H_5N_2Cl \cdot HgCl_2$. Calculated %: N 6.80

10. Reaction of potassium phenylazocarboxylate with arsenic trichloride in acetone, in an atmosphere of nitrogen. A suspension of 5 g of potassium phenylazocarboxylate in 100 ml of dry acetone was placed in a flask fitted with a dropping-funnel, and air was swept out by passing a stream of nitrogen for 20 minutes. A solution of 7.5 g of arsenic trichloride in 50 ml of dry acetone was then added gradually from the dropping funnel, without interrupting the flow of nitrogen, and with stirring. After completion of the reaction, the zinc dust test was negative, showing that the reaction mixture did not contain double salt of phenyldiazonium chloride and arsenic trichloride (gases not evolved). After a short contact of the mixture with air addition of zinc dust is followed by evolution of nitrogen, showing that the double diazonium salt has been formed.

SUMMARY

1. A method for the synthesis of aromatic arsenic-organic compounds through arylazocarboxylic salts is described.

2. The mechanism of the reactions involved is discussed.

3. It has been shown that arylazocarboxylic salts with arsenic trichloride in presence of air readily undergo conversion into double salts of aryldiazonium chloride and arsenic trichloride.

LITERATURE CITED

[1] A.N. Nesmeyanov and O.A. Reutov. Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci., No. 3, 316 (1948).
[2] O.A. Reutov and O.A. Ptitsina. ibid, No. 1, 93 (1952).*
[3] A.N Nesmeyanov and K.A. Kocheshkov. J. Gen. Chem., 4, 1102 (1934).
[4] Z. Földi, Ber., 56, 2489 (1923).
[5] I. Thiele, Ber. 28, 2600 (1895).
[6] A.N Nesmeyanov and O.A. Reutov. Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci., No. 6, 617 (1949).
[7] A. Michaelis, W. La Coste, Ann. 201, 184 (1880).
[8] F. Blicke, F. Smith, J. Am. Chem. Soc., 52, 2946 (1930).
[9] A. Michaelis, Ber. 11, 1888 (1878).
[10] W. La Coste, Ann. 208, 1 (1881).
[11] A. Hantzsch, O. Schultze, Ber. 28, 2077 (1895).
[12] A.F. Hunt, E. Turner, Trans. Chem. Soc. 127, 2667 (1925).
[13] H. Bart, Ann. 429, 101 (1922).
[14] O. Widman, Ber. 28, 1929 (1895).
[15] K.A. Kocheshkov and A.N. Nesmeyanov. J. Gen. Chem., 6, 144 (1936).
[16] A.P. Sabaneev J. Russ. Phys. Chem. Soc., 17, 176 (1885).
[17] A.N Nesmeyanov, Ber. 62, 1010 (1929).

Received June 1, 1952

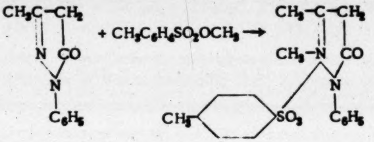
---

* See Consultants Bureau translation, p. 103.

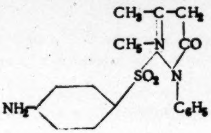
NEW DATA ON THE CHEMISTRY OF PYRAZOLONE DERIVATIVES

V. M. Rodionov and A. M. Fedorova

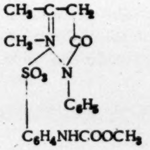
One of us [1] was able, during the course of a study of the conditions of synthesis of pyrazolone derivatives, to obtain in good yield the metho-p-toluenesulfonate of phenylmethylpyrazolone, by heating it with an equimolecular amount of methyl p-toluenesulfonate:



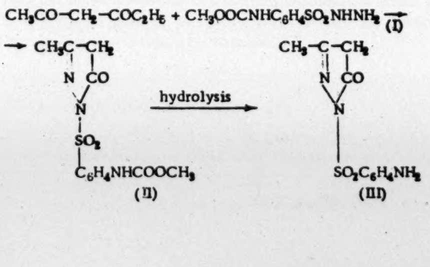
It would, for various reason, be of interest to investigate the analogous reaction with methyl p-aminobenzenesulfinate, and to prepare the metho-p-amino-benzenesulfinate of phenylmethylpyrazolone:



With this object we synthesized the carbomethoxy derivative of p-aminobenzenesulfinic acid, and prepared its methyl ester. However, a number of attempts at obtaining the product of addition of this ester to phenylmethylpyrazolone were unsuccessful, the ester always being recovered unchanged from the reaction. It is of interest that analogous experiments with methyl p-carbomethoxyaminobenzenesulfonate at once gave the expected addition product in good yield:



We next attempted to introduce the sulfamido group into the phenylmethylpyrazolone molecule in quite a different way. We know that a general method for preparing phenylmethylpyrazolone derivatives depends on condensation of phenylhydrazine with acetoacetic ester. Taking instead of hydrazine the hydrazide of p-carbomethoxyaminobenzene-sulfonic acid we hoped to obtain compound (III), of the desired structure:



As the starting material for this reaction we synthesized the hydrazide of carbomethoxyaminobenzenesulfonic acid (I) in 81-82% yield, by the action of hydrazine hydrate on an ethereal solution of the chloroanhydride of N-carbomethoxysulfanilic acid. This compound reacts with acetoacetic ester in alcohol or dry toluene or xylene to give the corresponding hydrazone, with subsequent ring closure, affording N-carbomethoxy-p-amino phenyl-N-methylpyrazolonesulfone (II).

Numerous attempts at hydrolyzing the carbomethoxy derivative to give the free amino derivative (III) were unsuccessful, owing to the extreme stability of the bond between the carbomethoxy residue and the amino group; the products obtained by heating with acids or alkalis are either the initial product recovered unchanged, or else products of total breakdown of the pyrazolone ring. The carbomethoxy derivative of the hydrazide of p-aminobenzenesulfonic acid was similarly resistant to acid or alkaline hydrolysis. Further study of this compound showed that in general it reacts readily with substances containing the carbonyl group. This is illustrated in the experimental section of this paper by the condensation products with benzaldehyde (IV) or acetone (V):

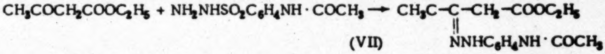
$$\underset{\text{(IV)}}{CH_3O_2C \cdot NHC_6H_4SO_2NHN = CHC_6H_5} \qquad \underset{\text{(V)}}{CH_3O_2C \cdot NHC_6H_4SO_2 \cdot NHN = C(CH_3)_2}$$

It is known that the acetyl group can usually be comparatively easily eliminated by hydrolysis, and we therefore decided to synthesize the hydrazide of N-acetylsulfanilic acid, in order to condense it with acetoacetic ester, so as to obtain compound (III).

The hydrazide (VI) of p-acetamidobenzenesulfonic acid was obtained in good yield (92-93%) by the action of hydrazine hydrate on the chloroanhydride of p-acetamidobenzenesulfonic acid:

$$\underset{\text{(VI)}}{CH_3CO \cdot NH \cdot C_6H_4SO_2NHNH_2}$$

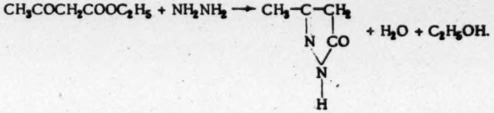
Condensation of this compound with acetoacetic ester gave only the corresponding hydrazone (VII) of acetoacetic ester, the second stage of the process, viz., elimination of alcohol with formation of the pyrazolone ring, not taking place:



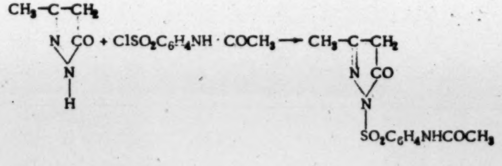
$$CH_3COCH_2COOC_2H_5 + NH_2NHSO_2C_6H_4NH \cdot COCH_3 \rightarrow \underset{\text{(VII)}}{CH_3C{-}\underset{\underset{NNHC_6H_4NH \cdot COCH_3}{\|}}{C}{-}CH_2{-}COOC_2H_5}$$

Unsuccessful attempts were made to synthesize the pyrazolone derivative by heating the hydrazone, either alone, or with various compounds able to combine with the alcohol liberated during ring closure; in all cases we either recovered the hydrazone unchanged, or else the products were uncrystallizable oils, attempts at fractional vacuum distillation of which led to production of a tarry mass.

These unsuccessful experiments obliged us to seek for other ways of synthesizing p-aminophenylmethylpyrazolonesulfone (III). The starting material was 3-methylpyrazolone, which was taken for condensation with the chloroanhydride of p-acetamidobenzenesulfonic acid. Methylpyrazolone was prepared according to Knorr [2], by reaction of acetoacetic ester with hydrazine hydrate:



The reaction proceeds smoothly in aqueous solution, and pure methylpyrazolone is obtained in one step, in ~ 80% yield. The product was condensed with the chloroanhydride of p-acetamidobenzenesulfonic acid, the best results being obtained in glacial acetic acid solution, in presence of anhydrous sodium acetate, when yields of ~ 65% of the acetyl derivative of the desired pyrazolone derivative were obtained:



Attempts at eliminating the acetyl group by hydrolysis showed that, similarly to the case of the carbomethoxy derivative, opening of the pyrazolone ring takes place very readily during hydrolysis. In this case, however, we found that when hydrolysis was conducted in acetone solution in presence of a small amount of hydrochloric acid the acetyl group is relatively readily eliminated, giving the free amino derivative in ~ 75% yield.

EXPERIMENTAL

Preparation of p-carbomethoxyaminobenzenesulfinic acid. $CH_3OOCNH \cdot C_6H_4SO_2H$

24.9 g of p-carbomethoxyaminobenzenesulfochloride (m.p. 108-110°) is added to 200 ml of a sodium sulfite solution obtained by mixing 50 ml of 36% aqueous $NaHSO_3$ with 150 ml of 5% aqueous sodium hydroxide, and the mixture is shaken for 2 hours, with occasional addition of caustic soda solution, so as to maintain an alkaline reaction (about 20 ml of 25% aq. NaOH). The mixture is then filtered, and the filtrate is made acid with 60% sulfuric acid, when the sulfinic acid separates as small colorless crystals, yield 19 g (83.7%), m.p. after one recrystallization from water 142-145°.

Found %: N 6.74.
$C_8H_9O_4NS$. Calculated %: N 6.51

Preparation of methyl p-carbomethoxyaminobenzenesulfinate through the silver salt of the sulfinic acid.

(a) Preparation of Ag salt. 15 g of p-carbomethoxyaminobenzenesulfinic acid is dissolved with heating in 148 ml of 2.5% aqueous sodium carbonate, and a solution of 11.8 g of silver nitrate in 150 ml of water is added to the hot solution, with vigorous stirring. The precipitate of Ag salt is drained on the filter-pump, and pressed on a porous tile, after which it is dried at 60°; yield 16 g (~ 71.5%).

Found %: Ag 33.41
$C_8H_8O_4NSAg$. Calculated %: Ag 33.51

(b) Preparation of methyl ester. 8.5 g (4 ml) of methyl iodide is added, with stirring, to 15.5 g of Ag salt in 100 ml of dry benzene, and the mixture is heated under reflux on the water bath for 2 hours. The hot solution is filtered, the residue of silver iodide is washed with a few portions of hot benzene, and the solvent is distilled off from the filtrate + washings. The residue melts at 173-182°, after recrystallization from methanol 182-183°; yield 7.3 g (66%).

Preparation of the methyl ester through the K salt of the sulfinic acid.

(a) Preparation of the K salt. A solution of 25 g of p-carbomethoxyaminobenzenesulfinic acid in 100 ml of 8% potassium carbonate is evaporated to dryness.

(b) Preparation of methyl ester. 10 g of methyl iodide is added gradually, with constant stirring, to 15 g of the K salt in 100 ml of methanol in a flask fitted with a reflux condenser, and placed on the water bath. Heating is continued for a further 2.5 hours, the hot solution is filtered, the solvent is distilled off from the filtrate, and the residue is recrystallized from methanol; yield of ester, m.p. 181-183°, 7.2 g (~ 53%).

Found %: C 47.37; H 4.70; N 6.42.
$C_9H_{11}O_4NS$ Calculated %: C 47.16; H 4.80; N 6.11.

All attempts at adding on this ester to phenylmethylpyrazolone, using the ordinary methods, were unsuccessful.

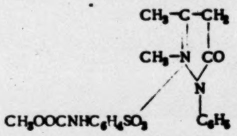
Preparation of methyl p-carbomethoxyaminobenzenesulfonate $CH_3OOCNH \cdot C_6H_4SO_3CH_3$.

A solution of sodium methoxide prepared from 5 g of sodium and 150 ml of methanol is added gradually from a dropping funnel to a cooled (not more than 10°) and well stirred solution of 48 g of p-carbomethoxyaminobenzenesulfochloride in 200 ml of methanol, cooling is continued for 2 hours, and the precipitate is collected and dried; yield of ester 38 g (80.5%), m.p. after one recrystallization from methanol 115-116°.

Found %: N 5.39
$C_9H_{11}O_5NS$. Calculated %: N 5.71

Substitution of 30% caustic soda for sodium methoxide gave lower yields of ester (60-65%).

Preparation of the addition product of the ester to phenylmethylpyrazolone



4.5 g of methyl p-carbomethoxybenzenesulfonate was heated with 3.5 g of phenylmethylpyrazolone for 30 minutes on an oil bath at 160°. The product was dissolved in water, and the solution was extracted with ether. The aqueous layer was evaporated to dryness on a water bath, and the residue was dissolved in ethanol. Addition of ether to the alcohol solution gave a white oily precipitate, which gradually crystallized, m.p. 58-60°.

Found %: C 52.86; H 5.42; N 9.37
$C_{19}H_{21}O_6N_3S$. Calculated %: C 54.4; H 5.2; N 10.02.

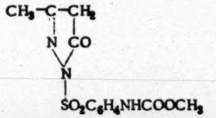
The product does not appear to be sufficiently pure, but there can be no doubt as to its structure.

Preparation of the hydrazide of p-carbomethoxyaminobenzenesulfonic acid. $CH_3O_2C \cdot NHC_6H_4SO_2NHNH_2$

100 g of sodium bicarbonate is added to a solution of 25 g of p-carbomethoxyaminobenzenesulfochloride in 250 ml of ether, followed by a solution of 5 g of hydrazine hydrate in 45 ml of ethanol, added from a dropping funnel, with vigorous stirring and cooling (10-15°). Stirring is continued for a further 2 hours, and the mixture is then left overnight. The precipitate is then collected, washed with ether, and then with soda solution, and dried at 45-50°; yield of hydrazide 19.9 g (81%), m.p. 170-173°, rising to 181-188° (decomposition) after recrystallization from alcohol.

Found %: C 39.12; 38.97; H 4.53; 4.59; N 16.84; 16.67
$C_9H_{11}O_4N_3S$. Calculated %: C 39.18; H 4.59; N 17.14

Preparation of p-carbomethoxyaminophenyl-N-3-methylpyrazolonesulfone



(a) 4.9 g of the hydrazide of p-carbomethoxyaminobenzenesulfonic acid is heated for 1 hour on the water bath with 3 ml of acetoacetic ester in 30 ml of alcohol, and the residue is recrystallized from 50 ml of alcohol, giving a product of m.p. 148-150°, raised to 156-158° by a second recrystallization from alcohol; yield 5 g (80.5% calculated on hydrazide taken).

(b) 4.9 g of hydrazide and 2.6 g of acetoacetic ester are mixed with 200 ml of dry toluene, and the solvent is distilled off, together with alcohol and water formed during condensation. The residue is recrystallized from alcohol, giving 5.6 g (90% yield, calculated on hydrazide) of product, m.p. 158-160°. Substitution of dry xylene for toluene lowered the yield to 70%.

Found %: N 13.63; 13.50
$C_{12}H_{13}O_5N_3S$. Calculated %: N 13.50

Preparation of the p-carbomethoxyaminophenylsulfonylhydrazone of benzaldehyde $CH_3OOC \cdot NHC_6H_4SO_2NHN{=}CHC_6H_5$.

4 ml of benzaldehyde is added to a hot solution of 10 g of the hydrazide of p-carbomethoxyaminobenzenesulfonic acid in 100 ml of alcohol, and the mixture is boiled under reflux for 1 hour. 8.8 g of the hydrazone crystallized from the cooled solution, m.p. 198-200°, yield about 64.7%.

Found %: C 54.77; 54.81; H 4.68; 4.70; N 12.98; 12.95
$C_{15}H_{15}O_4N_3S$. Calculated %: C 54.05; H 4.50; N 12.61

Preparation of the p-carbomethoxyaminophenylsulfonylhydrazone of acetone. $CH_3OOC\cdot NHC_6H_4SO_2NHN{=}C(CH_3)_2$.

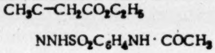
10 ml of acetone is added to a solution of 10 g of the hydrazide in 100 ml of glacial acetic acid at 50°, the solution is heated under reflux for 1 hour, and 59 ml of acetic acid is distilled off. 5 g of hydrazone crystallizes out from the cooled residue, m.p., after recrystallization from alcohol, 200-202°, yield 43%, calculated on hydrazide taken.

Found %: C 46.03; 46.15; H 5.24; 5.30; N 14.70; 14.86
$C_{11}H_{15}O_4N_3S$. Calculated %: C 46.31; H 5.26; N 14.73.

Preparation of the hydrazide of p-acetamidobenzenesulfonic acid. $CH_3CONHC_6H_4SO_2NHNH_2$

16 g of sodium bicarbonate is added to a solution of 20 g of p-acetamidobenzenesulfochloride in 400 ml of ether, followed by gradual addition of a solution of 20 g of hydrazine hydrate in 30 ml of methanol, with vigorous stirring. The mixture is left for 5 hours, and the precipitate is then collected, washed with ether and then with soda solution, and recrystallized from alcohol; yield of hydrazide 18.75 g, or 95.5%, calculated on acetamidobenzenesulfochloride taken.

Preparation of the hydrazone of acetoacetic ester derived from the hydrazide of p-acetamidobenzenesulfonic acid.

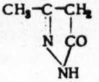


$$CH_3\underset{\displaystyle NNHSO_2C_6H_4NH\cdot COCH_3}{C}{-}CH_2CO_2C_2H_5$$

The solvent is distilled off from a solution of 3 g of the hydrazide and 1.7 ml of acetoacetic ester in 200 ml of dry benzene, and the residue is recrystallized from alcohol, giving the hydrazone, m.p. 118-120°, in 69% yield, calculated on hydrazide taken.

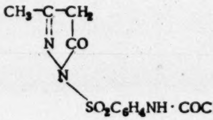
Found %: C 48.92; 49.03; H 6.00; 5.89; N 12.10; 12.21
$C_{19}H_{19}O_5N_3S'$. Calculated %: C 49.12; H 5.84; N 12.28

Preparation of methylpyrazolone



A solution of 27 ml of hydrazine hydrate in 135 ml of water is added drop by drop, with vigorous stirring, to a suspension of 65 g of acetoacetic ester in 130 ml of water, and the mixture is then heated on the water bath for 30 minutes under reflux. The cooled solution deposits methylpyrazolone, in large colorless crystals, m.p 210-213°, yield 38 g (77.5%).

Preparation of p-acetamidophenyl-N-methylpyrazolonesulfone



The yield of this reaction varies considerably according to the solvent taken. The reagents were taken in equimolecular amounts in all cases, and were heated: (a) in pyridine, (b) in acetone, (c) in glacial acetic acid; the respective yields were 30, 42 and 64%. We shall here describe only the third case.

18.6 g of p-acetamidobenzenesulfochloride, 7.85 g of methylpyrazolone, 8 g of anhydrous sodium acetate, and 100 ml of glacial acetic acid were heated under reflux for 2 hours, after which 200 ml of cold water were added to the clear solution. The crystalline product which separates is recrystallized from 50% alcohol, yield 15.3 g, or 64.2% of theory, calculated on methylpyrazolone taken.

Found %: C 48.54; 48.45; H 4.88; 4.91; N 14.24; 14.13
$C_{12}H_{13}O_4N_3S$. Calculated %: C 48.81; H 4.41; N 14.23

Hydrolysis of the acetyl derivative of pyrazolone.

Hydrolysis with dilute hydrochloric acid at low temperatures (75-80°) leads to opening of the pyrazolone ring, with production of sulfanilic acid, which separates from the cooled reaction mixture. The hydrolysis may, however, be effected smoothly in acetone solution in the presence of a small amount of hydrochloric acid. 3 g of acetyl derivative is heated for 1 hour on the water bath under reflux with 3 ml of 35% hydrochloric acid in 30 ml of acetone, the acetone is distilled off, and the residue is made alkaline with ammonia, and extracted with chloroform The extract gives 1.9 g of residue, a yield of 74%; the product melts at 152-155°, after recrystallization from 50% alcohol.

Found %: C 47.05; 46.96; H 4.90; 4.80; N 17.16; 17.11

$C_{10}H_{11}O_3N_3S$. Calculated %: C 47.43; H 4.34; N 16.66

SUMMARY

1. The synthesis of *p*-carbomethoxyaminobenzenesulfinic acid and of its methyl ester are described.

2. It was found that an adduct of this ester with phenylmethylpyrazolone could not be prepared, whereas methyl *p*-carbomethoxyaminobenzenesulfonate readily adds on to it.

3. The hydrazide of *p*-carbomethoxyaminobenzenesulfonic acid has been synthesized, and has been shown to function as a reagent for compounds containing the carbonyl group.

4. Condensation of the hydrazide of *p*-carbomethoxyaminobenzenesulfonic acid with acetoacetic ester gives *p*-carbomethoxyaminophenyl-N-methylpyrazolonesulfone.

5. Hydrolysis of the carbomethoxy derivative to the free amine does not take place in acid or alkaline solution. Heating either gives no effect, or involves opening of the pyrazolone ring.

6. The hydrazide of N-acetylsulfanilic acid reacts with acetoacetic ester to give only the corresponding hydrazone; the second stage of the reaction, involving formation of the pyrazolone ring, does not take place.

7. *p*-Acetamidophenyl-N-methylpyrazolonesulfone is prepared by condensing methylpyrazolone with *p*-acetamidobenzenesulfochloride.

8. Hydrolysis of the acetyl group of this sulfone does not take place under the ordinary conditions, but proceeds smoothly when it is heated with a small amount of hydrochloric acid in acetone solution.

LITERATURE CITED

[1] V.M. Rodionov, Bull. (4), 305 (1926).

[2] L. Knorr, Ber. 43, 2106 (1910).

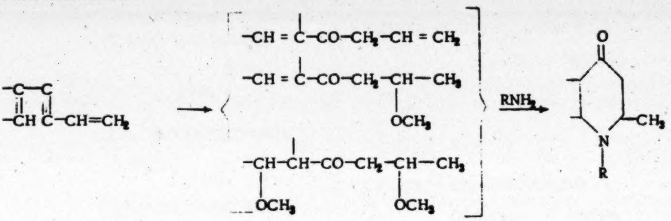
Received May 22, 1952.

ACETYLENE DERIVATIVES

PART 128. HETEROCYCLIC COMPOUNDS. XXIII. ACTION OF PRIMARY AROMATIC AMINES AND α-AMINOPYRIDINE ON VINYL ALLYL KETONES. SYNTHESIS OF ARYL-SUBSTITUTED γ-PIPERIDONES AND 1-(α-PYRIDYL)-4-PIPERIDONES

I. N. Nazarov, S. G. Matsoyan, and V. A. Rudenko

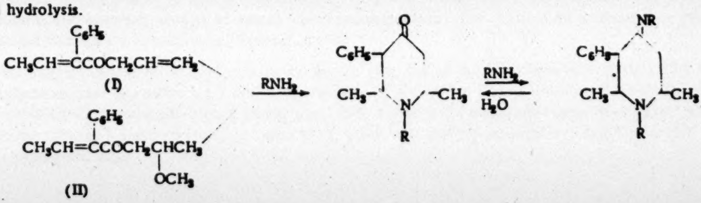
In 1948 a simple method was discovered in our laboratory for the synthesis of various 1-alkyl-4-piperidones [1], by the action of ammonia and primary alkylamines on vinyl allyl ketones and β-methoxy ketones, which are readily obtainable by the hydration of divinylacetylenic hydrocarbons in aqueous methanol solution, in presence of mercuric sulfate:



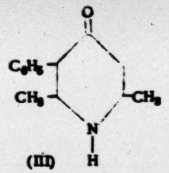
R = H or alkyl

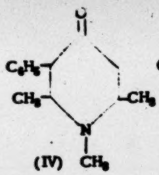
The 4-piperidones are the basic intermediates for the synthesis of physiologically active compounds of the piperidone series, having, similarly to the naturally occurring alkaloids of the morphine and tropane groups, analgesic, anesthetic, spasmolytic, and midriatic action. Starting with 4-piperidones, we have in our laboratory synthesized numerous 4-piperidone derivatives, in particular various esters of 4-piperidols, in order to discover new physiologically active substances, and to elucidate the connection between their structure and their analgesic action [2]. In connection with these studies we thought it necessary to extend the area of application of the reaction of cyclization of vinyl allyl ketones with amines, on the one hand taking dienones with aromatic substitutents, and on the other using aromatic amines. This would afford the possibility of achieving the synthesis of the little studied aryl-substituted γ-piperidones, in particular of those in which the aryl radical is substituted at the nitrogen atom.

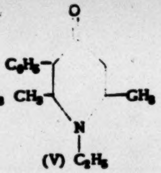
As was expected, ammonia, methylamine, and ethylamine react with mixtures of 3-phenylhepta-2,6-dien-4-one (I) and methoxyketone (II) to give the corresponding 5-phenyl-4-piperidones, and, by further reaction between 4-piperidones and primary amines, 4-iminopiperines are formed, which readily regenerate the initial 4-piperidones by acid hydrolysis.



We thus synthesized 5-phenyl-2,6-dimethyl-4-piperidone (III) (yield 55%), 5-phenyl-1,2,6-trimethyl-4-piperidone (IV) (yield 50%), and 5-phenyl-2,6-dimethyl-1-ethyl-4-piperidone (V) (isolated as the picrate); these are the first described members of the series of 5-aryl substituted 4-piperidones:

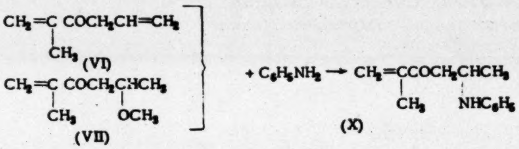

(III)


(IV)

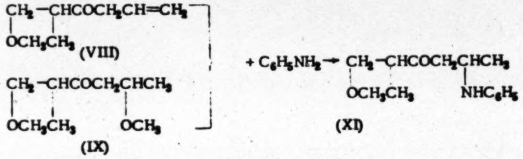

(V)

We next investigated the possibility of cyclization of vinyl allyl ketones with primary aromatic amines. We found that vinyl allyl ketones and their corresponding methoxyketones react in non-aqueous media with aromatic, as opposed to aliphatic, amines to give only addition products, which, similarly to other α,β-ketoarylamines, readily decompose when distilled.

Condensation of aniline with allyl isopropenyl ketone (VI) or with the methoxyketones (VII), (VIII), and (IX) gave β-anilinopropyl isopropenyl ketone (X) or β-anilinopropyl-β'-methoxyisopropyl ketone (XI), isolated as the picrates:

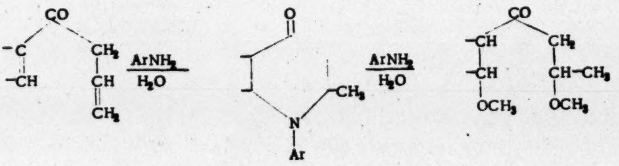


$$\left.\begin{array}{l} CH_2{=}C(CH_3)COCH_2CH{=}CH_2 \quad (VI) \\ CH_2{=}C(CH_3)COCH_2CH(OCH_3)CH_3 \quad (VII) \end{array}\right\} + C_6H_5NH_2 \rightarrow CH_2{=}C(CH_3)COCH_2CH(NHC_6H_5)CH_3 \quad (X)$$



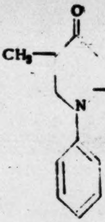
$$\left.\begin{array}{l} CH_3CH_2OCH_2CHCOCH_2CH{=}CH_2 \quad (VIII) \\ CH_3CH_2OCH_2CHCOCH_2CH(OCH_3)CH_3 \quad (IX) \end{array}\right\} + C_6H_5NH_2 \rightarrow CH_3CH_2OCH_2CHCOCH_2CH(NHC_6H_5)CH_3 \quad (XI)$$

A detailed study of the conditions under which these reactions proceed showed that cyclization of vinyl allyl ketones and of their corresponding β-methoxyketones with arylamines proceeds readily in presence of water, according to the following general scheme:

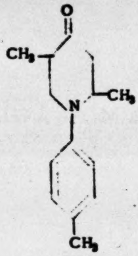


Addition products are, however, also found among the reaction products. The cyclization products were purified and isolated through the corresponding hydrochlorides.

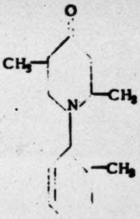
In this way, condensation of allyl isopropenyl ketone (VI), and of the methoxyketones (VII), (VIII) and (IX) with arylamines gave the following 1-aryl-4-piperidones: 1-phenyl-2,5-dimethyl-4-piperidone (XII), yield 45-50%, 1-*p*-tolyl-2,5-dimethyl-4-piperidone (XIII), yield 25%, 1-*o*-tolyl-2,5-dimethyl-4-piperidone (XIV), yield 30%, 1-*p*-methoxyphenyl-2,5-dimethyl-4-piperidone (XV), yield 58%, and 1-*p*-ethoxyphenyl-2,5-dimethyl-4-piperidone (XVI), yield 61%:



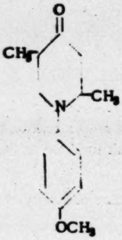
(XII)



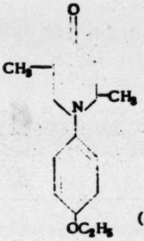
(XIII)



(XIV)

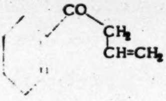


(XV)

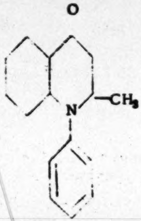


(XVI)

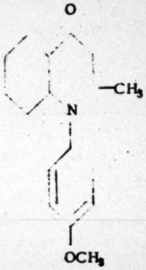
Condensation in presence of water of allyl Δ^1-cyclohexenyl ketone (XVII) with aniline or p-anisidine gave 1-phenyl-2-methyl-4-ketodecahydroquinoline (XVIII) and 1-p-methoxyphenyl-4-ketodecahydroquinoline (XIX), in ~40% yield:



(XVII)

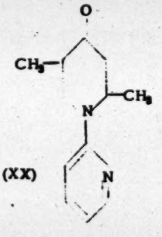


(XVIII)

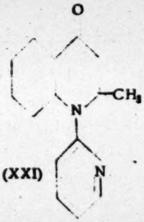


(XIX)

Condensation of α-aminopyridine with allyl isopropenyl ketone (VI) or allyl Δ^1-cyclohexenyl ketone (XVII) in presence of water gave ~ 30% yields of 1- α-pyridyl-2,5-dimethyl-4-piperidone (XX) and 1-α-pyridyl-2-methyl-4-ketodecahydroquinoline (XXI), belonging to the interesting group of bisheterocyclic systems:

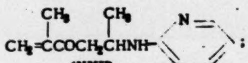


(XX)

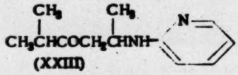


(XXI)

Under anhydrous conditions allyl isopropenyl ketone (VI) gives only the adduct (XXII), hydrogenation of which (Pd catalyst) gives the pyridylaminoketone (XXIII).



(XXII)



(XXIII)

As appears from the Table below, in the cyclization of vinyl isopropenyl ketone with arylamines the basic factor determining the direction of the reaction and the yield of cyclization products is the basicity of the given aromatic amine. The yield of γ-piperidone rises parallel with increase in the basicity (dissociation constant) of the amine.

Serial No.	Amine	Dissociation constant	% Yield of piperidone
1	p-Toluidine	$2 \cdot 10^{-10}$	25
2	o-Toluidine	$3.4 \cdot 10^{-10}$	30
3	Aniline	$5 \cdot 10^{-10}$	45-50
4	p-Anisidine	$1.5 \cdot 10^{-9}$	58
5	p-Phenetidine	$2.15 \cdot 10^{-9}$	61

The highest yield of piperidone was obtained with allyl isopropenyl ketone and p-phenetidine, which is the most basic ($2.15 \cdot 10^{-9}$) of the amines taken.

The aryl-substituted 4-piperidones obtained by us are all stable liquid or crystalline compounds, which can be distilled in vacuo without decomposition, and which readily give derivatives, at either the nitrogen atom or the carbonyl group.

EXPERIMENTAL

5-Phenyl-2,6-dimethyl-4-piperidone (III)

14 g of a mixture of 3-phenylhepta-2,6-dien-4-one (I) and methoxyketone (II) (b.p. 95-115° [1 mm, n_D^{20} 1.5320 [3]) were added to 23.2 ml of aqueous ammonia (d 0.93) and 45 ml of methanol, and the mixture was heated in a steel cylinder on a water-bath at 60-70° for 4 hours. The ammonia and methanol were then removed by vacuum evaporation, initially at room temperature, and later on a water-bath at 45°. The residue was made neutral with 1: 3 hydrochloric acid, and the neutral solution was exhaustively extracted with ether. The aqueous solution of salts of amines was treated with excess of solid alkali, and the brown oil separating was extracted with ether. The ethereal solution was dried with ignited potash, the ether was removed, and the dark-colored residue, which had partly crystallized, was vacuum distilled, giving 9 g of readily crystallizing product, b.p. 112° at 0.17 mm, m.p. 105-108°. Recrystallization from 50% alcohol gave 7.1 g of pure 5-phenyl-2,6-dimethyl-4-piperidone (III), colorless crystals, m.p. 108-109°.

Found %: N 6.82; 6.74
$C_{13}H_{17}ON$. Calculated %: N 6.88

Hydrochloride of 5-phenyl-2,6-dimethyl-4-piperidone. This was prepared by the action of hydrogen chloride on a solution of the base in absolute ether. After precipitation by absolute ether from alcohol it melted at 208-209° (decomposition).

Found %: N 5.61; 5.70
$C_{13}H_{18}ONCl$. Calculated %: N 5.84

The hydrochloride of the 2,4-dinitrophenylhydrazone was prepared by mixing alcoholic solutions of 5-phenyl-2,6-dimethyl-4-piperidone and 2,4-dinitrophenylhydrazine as yellow crystals (from methanol) m.p. 237-238° (decomposition).

The picrate of 5-phenyl-2,6-dimethyl-4-piperidone melted at 192-193° (from alcohol).

5-Phenyl-1,2,6-trimethyl-4-piperidone (IV)

12 ml of 34% aqueous methylamine and 50 ml of methanol were added to 10 g of a mixture of 3-phenylhepta-

2,6-dien-4-one (I), and the solution was heated for 8 hr in a sealed tube on a water bath at 70°. The product was subjected to the usual treatment. Excess methylamine was removed in vacuum, the residue was made neutral with dilute hydrochloric acid, neutral products were extracted with ether, the free base was liberated by adding potash, extracted with ether, and the extract was dried with magnesium sulfate. The ether was distilled off, and the residue was vacuum distilled, giving 6.2 g of liquid, b.p. 120-129° at 1 mm, n_D^{20} 1.5446, which has an unpleasant odor, and rapidly darkens on exposure to the air.

In order to free the base of admixture of imino-derivative it was dissolved in 10% hydrochloric acid, and the solution was heated on a boiling water-bath for 4 hrs. The free base was then liberated by adding sodium hydroxide, extracted with ether, the solution was dried with magnesium sulfate, the ether was distilled off, and the residue was vacuum distilled, giving 4.5 g of pure 5-phenyl-1,2,6-trimethyl-4-piperidone (IV), b.p. 119-121° at 1 mm, n_D^{20} 1.5420; d_4^{20} 1.0515; found MR_D 65.22; calculated MR_D 65.00.

Found %: C 77.87; 77.81; H 8.77; 8.72.
$C_{14}H_{19}ON$. Calculated %: C 77.48; H 8.75

The picrate of 5-phenyl -1,2,6-trimethyl-4-piperidone melts at 140-141° (from alcohol-acetone mixture).

Found %: N 12.66; 12.47
$C_{20}H_{22}O_8N_4$. Calculated %: N 12.55

5-Phenyl-2,6-dimethyl-1-ethyl-4-piperidone (V)

10 g of a mixture of 3-phenylhepta-2,6-dien-4-one (I) with its corresponding methoxyketone (II) (b.p. 80-106° at 1 mm, n_D^{20} 1.551) and 10 ml of 50% aqueous ethylamine in 15 ml of methanol (for full dissolution of the ketones) were heated for 2 hrs in a sealed tube in a water-bath at 65-70°. The reaction product was treated in the same way as before, and vacuum distillation of the base obtained gave the following fractions:

Fraction I, b.p. 80-89° at 0.25 mm; n_D^{20} 1.5478; 1.7 g.
Fraction II, b.p. 90-100° at 0.2 mm; n_D^{20} 1.5475; 2.8 g.
Fraction III, b.p. 100-105° at 0.2 mm; n_D^{20} 1.5400; 0.8 g.

All the fractions had an unpleasant, mousy odor, due to the imino-ketone, and rapidly darken when exposed to the air. Addition to Fraction II of a saturated alcoholic solution of 3 g of picric acid gave a dark-colored precipitate of picrate, which after 2 recrystallizations from alcohol-acetone gave 2.7 g of the picrate of 5-phenyl-2,6-dimethyl-1-ethyl-4-piperidone (V), m.p. 150-151°.

Found %: N 11.85; 12.01
$C_{21}H_{24}O_8N_4$. Calculated %: N 12.16

1-Phenyl-2,5-dimethyl-4-piperidone (XII)

a) Action of aniline on allyl isopropenyl ketone (VI) in presence of water. 250 ml of dioxan was added to a boiling mixture (under reflux) of 110 g of allyl isopropenyl ketone (b.p. 48-50° at 12 mm, n_D^{20} 1.4691) [4], 93 g of freshly distilled aniline, and 60 ml of water, and the homogeneous solution was boiled for 23 hrs, during which time a liquid phase separated in increasing amount. The system was acidified with 1:1 hydrochloric acid, the dioxan and water were distilled off in vacuo, and the residue of salts of amines was dissolved in 200 ml of hot water. The cooled solution was extracted with ether, to remove neutral products, and it was then made alkaline with solid alkali. The dark-colored mass separating was extracted with ether, and the solution was dried with sodium sulfate, and fractionally distilled, giving the fractions:

Fraction I, b.p. 60-115° at 1 mm; 11.5 g
Fraction II, b.p. 115-130° at 1 mm; 150.7 g
Fraction III, b.p. 130-160° at 1 mm; 10.1 g (with decomposition)
Tarry residue — 22 g

Fraction II (b.p. 115-130° at 1 mm) was dissolved in 300 ml of 1:1 hydrochloric acid, and the solution was evaporated to dryness on a water-bath, in vacuo. The partly crystalline residue was treated with warm acetone, to purify the crystals of hydrochloride, which were then collected on the filter (145 g), washed with ether, and dissolved in water. Excess of alkali was added to the solution of hydrochloride, and the oil separating was again extracted with ether, the ethereal solution was dried with sodium sulfate, the ether was distilled off, and the residue was vacuum distilled, giving 102 g of 1-phenyl-2,5-dimethyl-4-piperidone (XII), a colorless, viscous oil, insoluble in water, with a faint odor of aniline, b.p. 116-117° at 1 mm, n_D^{22} 1.5519, d_4^{22} 1.0650, experimental MR_D 60.98, calculated MR_D 60.55.

Found %: N 6.97; 6.91
$C_{13}H_{17}ON$. Calculated %: N 6.88

The hydrochloride of 1-phenyl-2,5-dimethyl-4-piperidone was prepared by passing dry hydrogen chloride through an ethereal solution of the base. It is readily soluble in water, but not in acetone. After recrystallization from alcohol-acetone mixture it melts at 157-157.5° (in a sealed capillary).

Found %: N 6.11; 5.88
$C_{13}H_{18}ONCl$. Calculated %: N 5.84
Found %: Cl 14.96
$C_{13}H_{18}ONCl$. Calculated %: Cl 14.80

The picrate of 1-phenyl-2,5-dimethyl-4-piperidone was prepared by mixing alcoholic solutions of picric acid and of the base; yellow crystals, insoluble in alcohol, m.p. 137-138°.

Found %: N 13.13; 12.95; 12.92
$C_{19}H_{20}O_8N_4$. Calculated %: N 12.96

The hydrochloride of the dinitrophenylhydrazone was prepared by adding an acid alcoholic solution of 2,4-dinitrophenylhydrazine to an alcoholic solution of 1-phenyl-2,5-dimethyl-4-piperidone; m.p. 183-183.5° (from alcohol).

Found %: N 16.48; 16.63
$C_{19}H_{22}N_5O_4Cl$. Calculated %: N 16.68

The acetone was distilled off from the filtrate from 1-phenyl-2,5-dimethyl-4-piperidone hydrochloride, and the dark, non-crystalline residue was dissolved in a small volume of water. The solution was alkalized, the base separating was extracted with ether, and the extract was dried with sodium sulfate. Repeated fractional distillation in vacuo, which was associated with decomposition of the product, gave 6.5 g of base, b.p. 124-128° at 1 mm, a light yellow liquid with an odor resembling that of the initial dienone. Addition of a saturated alcoholic solution of picric acid (7 g) to an alcoholic solution of the base gave a yellow oil, from which a crystalline picrate was obtained by treatment with acetone-alcohol mixture. Fractional crystallization of the picrate from an ethanol-methyl ethyl ketone mixture gave 1.2 g of the picrate of β-anilinopropyl isopropenyl ketone (X), m.p. 125-126°.

Found %: N 13.1; 12.76
$C_{19}H_{20}O_8N_4$. Calculated %: N 12.96

b) Action of aniline on a mixture of methoxyketones (VII), (VIII), and (IX) in presence of water. 130 g of a mixture of the methoxyketones (VII), (VIII), and (IX) (b.p. 65-85° at 13 mm, n_D^{20} 1.4350) [4], 150 g of aniline, and 200 ml of water were heated to boiling under reflux, and 160 ml of methanol was added; the homogeneous solution was boiled for 22 hrs. The oily layer of base which separated from the cooled solution was dissolved by adding 200 ml of concentrated hydrochloric acid, and the acid solution was extracted with ether, to remove neutral products, and was then evaporated in vacuo. The semi-crystalline residue was repeatedly extracted with acetone, and the crystalline hydrochloride remaining was collected on the filter, and washed with ether.

The hydrochloride (125 g) was dissolved in water, and the solution was made alkaline. The oily layer separating was extracted with ether, dried with sodium sulfate, and vacuum distilled. Repeated distillation gave 82 g of the above-described 1-phenyl-2,5-dimethyl-4-piperidone (XII), b.p. 116-117° at 1 mm, n_D^{21} 1.5520, the picrate of which, m.p. 137.5-138°, gave no depression with the previous specimen.

c) Action of aniline on a mixture of the methoxyketones (VII), (VIII), and (IX), in absence of water. A mixture of 70 g of the methoxyketones (VII), (VIII), and (IX) (b.p. 65°-85° at 13 mm, n_D^{20} 1.4350), 60 g of freshly distilled aniline, and 75 ml of anhydrous dioxan was boiled under reflux for 25 hrs, and the dioxan and unreacted reagents were distilled off in vacuo. Partial decomposition of the tarry residue (90 g) took place during its vacuum distillation. Repeated redistillation finally gave 11 g of product, b.p. 122-126° at 1 mm, n_D^{20} 1.5560.

An alcoholic solution of the product was left overnight with a saturated alcoholic solution of picric acid (12 g), giving 1.3 g of picrate, m.p. 137-139°, not giving any depression with the picrate of 1-phenyl-2,5-dimethyl-4-piperidone. The mother liquor, after removal of part of the solvent, gave 4.5 g of the picrate of β-anilinopropyl β-methoxyisopropyl ketone (XI), m.p. 104-105° (from alcohol).

Found %: N 12.14; 11.90

$C_{20}H_{24}O_9N_4$. Calculated %: N 12.06

The base liberated from the picrate of m.p. 104-105° underwent decomposition when distilled; no individual products could be isolated from the distillate.

1-p-Tolyl-2,5-dimethyl-4-piperidone (XIII)

A solution of 93 g of a mixture of allyl isopropenyl ketone (VI) with the corresponding methoxyketones (VII), (VIII), and (IX) (b.p. 55-80° at 12 mm, n_D^{21} 1.4281) in 200 ml of methanol was added gradually to a boiling emulsion of 100 g of p-toluidine (freshly distilled) in 300 ml of water, and boiling was continued under reflux for 24 hrs., after which 120 ml of concentrated hydrochloric acid was added to the cooled solution, which was then evaporated down under reduced pressure, and extracted with ether, to remove neutral products. The solution was saturated with solid caustic soda, the oil separating was twice extracted with ether, the ether solution was dried with sodium sulfate, the ether was distilled off, and the residue was fractionally distilled in vacuo. An ethereal solution of the fraction (56 g) boiling at 137-143° at 1.5 mm was saturated with hydrogen chloride, the hydrochloride which separated was collected, washed with acetone, and recrystallized from alcohol containing a small amount of water, giving 42 g of 1-p-tolyl-2,5-dimethyl-4-piperidone hydrochloride, glistening crystals, m.p. 158.5-160° (decomposition).

Found %: N 5.52; 5.58

$C_{14}H_{20}ONCl$ Calculated %: N 5.52

Addition of aqueous potassium carbonate to an aqueous solution of the hydrochloride of m.p. 158.5-160° gave 1-p-tolyl-2,5-dimethyl-4-piperidone (XIII), b.p. 128° at 1 mm, n_D^{20} 1.5419; d_4^{20} 1.0420; found MR_D 65.5; calculated MR_D 65.17, a colorless, viscous liquid, which can be distilled without decomposition.

Found %: N 6.94; 6.81

$C_{14}H_{19}ON$. Calculated %: N 6.45

1-o-Tolyl-2,5-dimethyl-4-piperidone (XIV)

A mixture of 95 g of allyl isopropenyl ketone (VI) with its corresponding methoxyketones (VII), (VIII), and (IX) (b.p. 55-80° at 12 mm, n_D^{21} 1.4281), 100 g of freshly distilled o-toluidine, 300 ml of water, and 250 ml of methanol was boiled for 21 hrs. The methanol was then distilled off in vacuo, the solution was acidified with concentrated hydrochloric acid, and the solution was extracted with ether, to remove neutral products. The free base was liberated by adding solid alkali, and was extracted with ether, the ethereal solution was dried with sodium sulfate, the ether was distilled off, and the residue was vacuum distilled. An ethereal solution of the fraction boiling at 120-130° at 1 mm (67 g) was saturated with dry hydrogen chloride, the mixture of salts obtained was washed with acetone, and the residual material was recrystallized from 90% ethanol, giving 50.5 g of 1-o-tolyl-2,5-dimethyl-4-piperidone hydrochloride, m.p. 132.5-133.5°.

Found %: N 5.83; 5.79

$C_{14}H_{20}ONCl$. Calculated %: N 5.52

Alkalization of an aqueous solution of the hydrochloride gave the free base 1-o-tolyl-2,5-dimethyl-4-piperidone (XIV), b.p. 107° at 0.5 mm, n_D^{20} 1.5288; d_4^{20} 1.0231; found MR_D 65.48; calculated MR_D 65.17, a colorless, viscous liquid, which can be distilled without decomposition.

Found %: N 6.87; 6.90

$C_{14}H_{19}ON$. Calculated %: N 6.45

1-p-methoxyphenyl-2,5-dimethyl-4-piperidone (XV)

A mixture of 100 g of allyl isopropenyl ketone (VI) with its corresponding methoxyketones (VII), (VIII), and (IX) (b.p. 55-80° at 12 mm, n_D^{21} 1.4281), 160 g of p-anisidine, 100 ml of water, and 170 ml of methanol was boiled under reflux for 25 hrs. The methanol was then distilled off in vacuo, the residue was made acid with 150 ml of concentrated hydrochloric acid, and the solution was extracted with ether to remove neutral products. The aqueous solution was evaporated to dryness in vacuo, and the residue was boiled for 2 hrs under reflux with 200 ml of acetone. The crystalline product was collected, washed with ether, and recrystallized from acetone containing a small amount of alcohol, giving 175 g of 1-p-methoxyphenyl-2,5-dimethyl-4-piperidone hydrochloride, m.p. 152.5-153.5°.

Found %: N 5.62; 5.50

$C_{14}H_{20}O_2NCl$. Calculated %: N 5.20

Addition of aqueous ammonia to an aqueous solution of the hydrochloride (m.p. 152.5-153.5°) gave the free base 1-p-methoxyphenyl-2,5-dimethyl-4-piperidone (XV), colorless crystals (from light petroleum), m.p. 51.5-52.5°, b.p. 124-125° at 0.5 mm.

Found %: N 6.11; 6.31
$C_{14}H_{19}O_2N$. Calculated %: N 6.04

The hydrochloride of the dinitrophenylhydrazone was obtained by adding an alcoholic solution, acidified with hydrochloric acid, of 2,4-dinitrophenylhydrazine to an alcoholic solution of 1-p-methoxyphenyl-2,5-dimethyl-4-piperidone; it melts at 188-188.5° (from alcohol).

Found %: N 15.46; 15.70
$C_{20}H_{24}O_5N_5Cl$. Calculated %: N 15.55

1-p-Ethoxyphenyl-2,5-dimethyl-4-piperidone (XVI)

A mixture of 35 g of allyl isopropenyl ketone (VI) with its corresponding methoxyketones (VII), (VIII), and (IX) (b.p. 55-80° at 12 mm, n_D^{21} 1.4281), 35 g of p-phenetidine, 20 ml of water, and 20 ml of methanol was boiled under reflux for 21 hrs, and the dark, oily layer of base formed was separated, treated with 50 ml of concentrated hydrochloric acid, and extracted with ether, to remove neutral products. The aqueous layer was then cooled, when 9 g of phenetidine hydrochloride (m.p. 232-234°) separated. It was filtered off, and the filtrate was alkalized with solid alkali, when an oil separated, which crystallized when cooled. It was collected, dried, and recrystallized from alcohol, giving 37 g of 1-p-ethoxyphenyl-2,5-dimethyl-4-piperidone (XVI), large crystals, m.p. 87-88°.

Found %: N 5.89; 6.07
$C_{15}H_{21}O_2N$. Calculated %: N 5.67

The hydrochloride of 1-p-ethoxyphenyl-2,5-dimethyl-4-piperidone was precipitated as an oil when an ethereal solution of the base was saturated with dry hydrogen chloride. The oil was dissolved in hot methyl ethyl ketone, and the cooled solution deposited the crystalline hydrochloride, m.p. 129-130°.

Found %: N 5.28; 5.25
$C_{15}H_{22}O_2NCl$ Calculated %: N 4.93

1-α-pyridyl-2,5-dimethyl-4-piperidone (XX)

a) Action of α-aminopyridine on a mixture of methoxyketones (VII), (VIII), and (IX), in presence of water. A mixture of 100 g of methoxyketones (VII), (VIII), and (IX) (b.p. 55-80° at 12 mm, n_D^{21} 1.4281), 100 g of α-aminopyridine, and 400 ml of water was boiled for 5 hrs, and the oily layer separating from the cooled solution was separated and vacuum distilled, giving 65 g of distillate boiling at 120-125° at 1 mm, a viscous liquid, darkening on exposure to the air, and possessing an unpleasant odor. The hydrochloride obtained by saturating an ethereal solution of the fraction with hydrogen chloride was extracted a few times with hot acetone, and was then twice precipitated from alcohol by means of ether, giving 55 g of monohydrochloride of 1-α-pyridyl-2,5-dimethyl-4-piperidone, m.p. 149-150°.

Found %: N 11.74; 11.90; Cl 14.48
$C_{12}H_{17}N_2OCl$. Calculated %: N 11.60; Cl 14.75

Alkalization of an aqueous solution of the hydrochloride gave the free base 1-α-pyridyl-2,5-dimethyl-4-piperidone (XX), m.p. 70-71° (from light petroleum), b.p. 112° at 0.5 mm, small odorless crystals, insoluble in water.

Found %: N 13.60; 13.90
$C_{12}H_{16}N_2O$. Calculated %: N 13.72

b) Action of α-aminopyridine on allyl isopropenyl ketone (VI) in absence of water. A mixture of 15 g of allyl isopropenyl ketone (b.p. 43-46° at 11 mm, n_D^{20} 1.4705) and 12 g of α-aminopyridine (m.p. 57°) was heated for 20 min. on a boiling water-bath, and the mixture was then fractionally distilled in vacuum. The following fractions were obtained, after the unchanged reagents had been distilled off (6.8 g of allyl isopropenyl ketone and 4.4 g of α-aminopyridine):

Fraction I, b.p. 73-126° at 3 mm; 2.6 g
Fraction II, b.p. 127-129° at 3 mm; 8.2 g; n_D^{20} 1.5580.

Fraction I partly crystallized, and the crystals were found to be α-aminopyridine, m.p. 57°. Fraction II is a viscous, yellow liquid, with a sharp, unpleasant odor; it rapidly darkens on standing. Redistillation of Fraction II gave the fractions:

Fraction I, b.p. 45-49° at 11 mm, 1.0 g; n_D^{20} 1.4700
Fraction II, b.p. 70-128° at 2.5 mm; 2.2 g;
Fraction III, b.p. 129-131° at 2.5 mm; 2.5 g; n_D^{20} 1.5575

Fraction I is allyl isopropenyl ketone, and the crystals separating from Fraction II were found to be α-aminopyridine, m.p. 57°.

Thus the product of reaction of allyl isopropenyl ketone with α-aminopyridine, in absence of water, decomposes when vacuum distilled, regenerating the initial reagents; it is β-(α-aminopyridino)-propyl isopropenyl ketone (XXII), b.p. 129-131° at 2.5 mm, n_D^{20} 1.5575; d_D^{20} 1.0554; found MR_D 62.27; calculated MR_D 60.30, the picrate of which melts at ~230° (decomposition) (from alcohol).

The same product, β-(α-aminopyridino)-propyl isopropenyl ketone (XXII), is obtained when a mixture of methoxyketones (VII) and (VIII) is heated in absence of water. The theoretical amount of hydrogen was absorbed when 4.5 g of this product in 10 ml of alcohol was hydrogenated with Pd catalyst at room temperature. The alcohol was then distilled off, and the residue was twice distilled in vacuum, giving 1.3 g of β-(α-aminopyridino)-propyl isopropyl ketone (XXIII), a faint yellow liquid, b.p. 125-126° at 4 mm, n_D^{20} 1.5280; d_4^{20} 1.0243; found MR_D 61.98; calculated MR_D 60.77; picrate, m.p. 130-131° (from alcohol)

1-Phenyl-2-methyl-4-ketodecahydroquinoline (XVIII)

A mixture of 28 g of allyl Δ^1-cyclohexenyl ketone (XVII) (b.p. 108° at 9 mm, n_D^{20} 1.5102) [5] 27 g aniline, 65 ml of water, and 120 ml of dioxan was boiled under reflux for 15 hrs, and the oily product separating after cooling was vacuum distilled, giving 27 g of a fraction, b.p. 140-146° at 1 mm, which crystallized on standing. Recrystallization from light petroleum gave 15.3 g of 1-phenyl-2-methyl-4-ketodecahydroquinoline (XVIII), large crystals, insoluble in water, m.p. 101-103°.

Found %: N 5.77; 5.97
$C_{16}H_{21}ON$. Calculated %: N 5.75

The hydrochloride of 1-phenyl-2-methyl-4-ketodecahydroquinoline was obtained by saturating an ethereal solution of the base with dry hydrogen chloride; after recrystallization from alcohol-ether mixture it had m.p. 142-143°.

Found %: N 5.17; 5.27
$C_{16}H_{22}ONCl$. Calculated %: N 5.00

1-p-Methoxyphenyl-2-methyl-4-ketodecahydroquinoline (XIX)

A mixture of 20 g of allyl Δ^1-cyclohexenyl ketone (XVII) (b.p. 108° at 9 mm, n_D^{20} 1.5102), 18 g of p-anisidine, 13 ml of water, and 18 ml of methanol was boiled under reflux for 12 hrs, and the dark oil which separated on cooling was distilled in vacuum. The fraction (20g) of b.p. 145-160° at 1 mm was dissolved in ether, and the solution was saturated with dry hydrogen chloride. The mixture of salts so obtained was washed with acetone, and recrystallized from alcohol-methyl ethyl ketone mixture, giving 16.5 g of 1-p-methoxyphenyl-2-methyl-4-ketodecahydroquinoline hydrochloride, m.p. 150-151°.

Found %: N 4.83; 4.71
$C_{17}H_{24}O_2NCl$. Calculated %: N 4.52

Addition of aqueous ammonia to an aqueous solution of the hydrochloride gave colorless, odorless crystals of 1-p-methoxyphenyl-2-methyl-4-ketodecahydroquinoline (XIX), m.p. 98-99°, insoluble in water.

Found %: N 5.31; 5.25
$C_{17}H_{23}O_2N$. Calculated %: N 5.12

1-α-Pyridyl-2-methyl-4-ketodecahydroquinoline (XXI)

A solution of 10 g of allyl Δ^1-cyclohexenyl ketone (XVII) (b.p. 108° at 9 mm, n_D^{20} 1.5102), 16 ml of water, and 11 g of α-aminopyridine was boiled under reflux for 22 hrs, and the dark oil separating from the cooled solution was vacuum distilled. The fraction (6.1 g) boiling at 155-160° at 1 mm was dissolved in alcohol, and an alcoholic solution of 6 g of picric acid was added. The product was recrystallized from alcohol-acetone mixture, giving 5.2 g of the monopicrate of 1-α-pyridyl-2-methyl-4-ketodecahydroquinoline (XXI), a yellow powder, m.p. 145-146°.

Found %: N 14.90; 14.85
$C_{21}H_{23}O_8N_5$. Calculated %: N 14.80

SUMMARY

1. New 5-phenyl-4-piperidones have been prepared by cyclization of 3-phenylhepta-2,6-dien-4-one with ammonia, methylamine, and ethylamine. In contrast to aliphatic amines, aromatic amines react with vinyl allyl ketones in absence of water to give only addition products. Cyclization of allyl isopropenyl ketone and allyl Δ^1-cyclohexenyl ketone with primary aromatic amines or α-aminopyridine is effected in presence of water.

2. A general method is advanced for the preparation of 1-aryl-4-piperidones and 1-α-pyridyl-4-piperidones.

3. The yield of cyclization product is shown to be proportional to the basicity of the aromatic amine taken.

Received April 15, 1952

Institute of Organic Chemistry
Academy of Sciences USSR

LITERATURE CITED

[1] I. N. Nazarov and V. A. Rudenko. Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 6, 610 (1948).

[2] I. N. Nazarov, V. Ya. Raigorodskaya, and V. A. Rudenko, Bull Acad. Sci. USSR, Div. Chem. Sci., No. 5, 504 (1949).

[3] I. N. Nazarov and I. L. Kotlyarevsky, J. Gen. Chem., 18, 912 (1948).

[4] I. N. Nazarov and I. I. Zaretskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 1, 211 (1941).

[5] I. N. Nazarov and L. N. Pinkina, Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 6, 633 (1946).

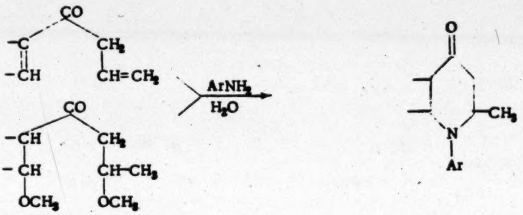
ACETYLENE DERIVATIVES

PART 129. HETEROCYCLIC COMPOUNDS

XXIV. TRANSFORMATIONS OF 1-PHENYL-2,5-DIMETHYL-4-PIPERIDONE

I. N. Nazarov, S. G. Matsoyan, and V. A. Rudenko

The preceding paper described the synthesis of 1-aryl-4-piperidones, which are readily formed by cyclization of vinyl allyl ketones or of their corresponding β-methoxyketones with primary aromatic amines, in presence of water [1]:



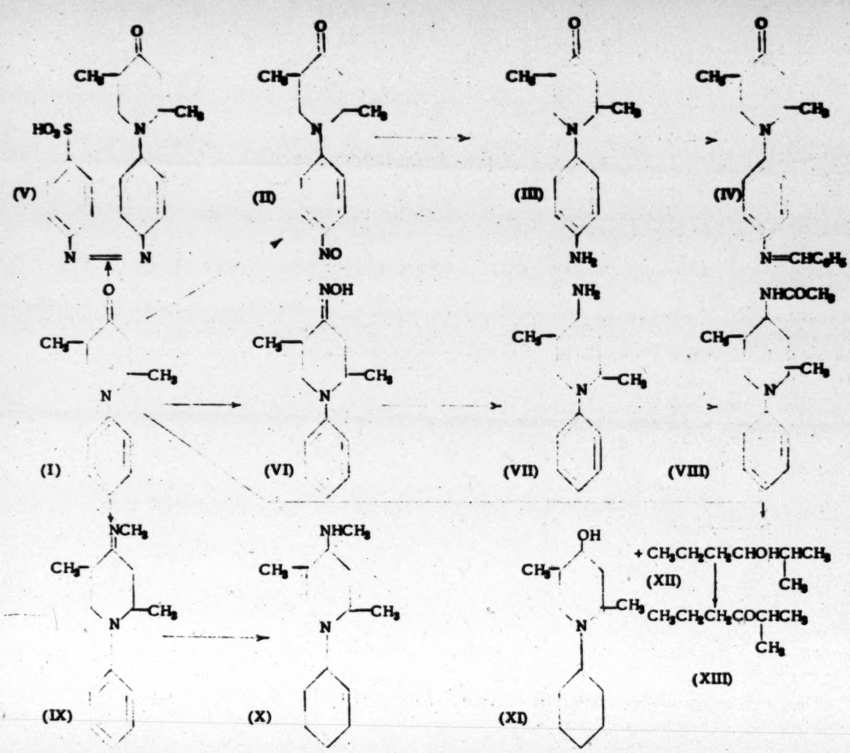
N-Aryl-4-piperidones have been little studied up till now, because of the difficulty of their preparation. The only known representatives of this group were 1-phenyl-4-piperidone (only the hydrochloride was described) [2] and 1,2,6-triphenyl-4-piperidone [3].

The simple and general method for synthesis of 1-aryl-4-piperidones described by us afforded us the opportunity of studying various reactions of 1-phenyl-2,5-dimethyl-4-piperidone (I), which is readily prepared from the commercially obtainable methylvinylethinylcarbinol and aniline. 1-Phenyl-2,5-dimethyl-4-piperidone (I), similarly to dialkylanilines, reacts in the cold with nitrous acid, giving 1-p-nitrosophenyl-2,5-dimethyl-4-piperidone (II) in 73% yield; green granules with a metallic sheen. This nitroso-compound is reduced by stannous chloride in hydrochloric acid solution to 1-p-aminophenyl-2,5-dimethyl-4-piperidone (III) (96% yield), which, in the same way as other aromatic amines, readily condenses with benzaldehyde, giving a 68% yield of the Schiff's base 1-p-benzylideneaminophenyl-2,5-dimethyl-4-piperidone (IV).

1-Phenyl-2,5-dimethyl-4-piperidone (I) readily couples with p-diazobenzenesulfonic acid, giving the azo-dye (V) in 66% yield. Its sodium salt resembles methyl orange in giving yellow aqueous solutions which change to an intense red when the solution is acidified.

Addition of hydroxylamine to an aqueous alcoholic solution of 1-phenyl-2,5-dimethyl-4-piperidone (I) gives a quantitative yield of the oxime (VI), as a mixture of stereoisomeric syn- and anti-isomers, which we were not able to separate by means of fractional crystallization. Reduction of oxime (VI) gave the expected 4-amino-1-phenyl-2,5-dimethylpiperidine (VII), which avidly absorbs atmospheric carbon dioxide, affording the carbonate. The primary amine (VII) (or its carbonate) is easily acetylated with acetic anhydride, giving 4-acetamido-1-phenyl-2,5-dimethylpiperidine (VIII).

Condensation of 1-phenyl-2,5-dimethyl-4-piperidone (I) with methylamine gives 4-methylimino-1-phenyl-2,5-dimethylpiperidine (IX), a liquid which darkens when exposed to the air, and which possesses the characteristic unpleasant odor of imines. Hydrogenation of this imine (Pd catalyst) affords 4-methylamino-1-phenyl-2,5-dimethylpiperidine (X): (see top of next page).



Exhaustive hydrogenation under pressure (200-250°; 90 atm), with Raney Ni catalyst, converts 1-phenyl-2,5-dimethyl-4-piperidone (I) into the known 1-cyclohexyl-2,5-dimethyl-4-piperidol (XI), together with products of opening of the piperidine ring. The low b.p. fraction, after elimination of basic compounds, was found to contain 2-methyl-hexan-3-ol (XII), identified as the semicarbazone of 2-methylhexan-3-one (XIII). It follows that the piperidine ring ruptures at the nitrogen atom.

EXPERIMENTAL

1-Phenyl-2,5-dimethyl-4-piperidone (I) was prepared by the method given in our preceding paper [1], by the cyclization of allyl isopropenyl ketone and its corresponding methoxyketones with aniline, in presence of water.

1-p-Nitrosophenyl-2,5-dimethyl-4-piperidone (II). 24 g of 1-phenyl-2,5-dimethyl-4-piperidone (b.p. 116-118° at 1 mm, n_D^{20} 1.5521) was dissolved in 98 ml of 1:1 hydrochloric acid, in a porcelain beaker. The beaker was cooled in ice, 50 g of ice was added to it, and a cooled solution of 9.5 g of sodium nitrite in 40 ml of water was added drop by drop, from a dropping funnel, with energetic shaking. The hydrochloride which separates after an hour was collected, and the filtrate was concentrated, when a further batch of hydrochloride crystallized out. After recrystallization from a mixture of concentrated hydrochloric acid and alcohol 23.2 g of 1-p-nitrosophenyl-2,5-dimethyl-4-piperidone hydrochloride was obtained; well-formed orange-yellow crystals, m.p. 152-153°.

The free base was obtained by shaking a mixture of the hydrochloride with ether and aqueous sodium carbonate, separating the emerald green ethereal layer, and evaporating off the solvent in a porcelain dish. The mixture was recrystallized from an alcohol-gasoline mixture, to give 1-p-nitrosophenyl-2,5-dimethyl-4-

piperidone (II), m.p. 130-130.5°, small green crystals with a metallic sheen.

Found %: N 11.97; 12.14
$C_{13}H_{16}O_2N_2$. Calculated %: N 12.06

1-p-Nitrosophenyl-2,5-dimethyl-4-piperidone is instantly hydrolyzed by aqueous alkalis, with production of p-nitrosophenol and 2,5-dimethyl-4-piperidone, which undergoes condensation under the conditions of the reaction. p-Nitrosophenol is identified by the Liberman reaction, after separation from the tarry products.

1-p-Aminophenyl-2,5-dimethyl-4-piperidone (III). A solution of 1-p-nitrosophenyl-2,5-dimethyl-4-piperidone hydrochloride, prepared as above from 18 g of 1-p-phenyl-2,5-dimethyl-4-piperidone, 75 ml of hydrochloric acid, and 7.5 g of sodium nitrite in 50 ml of water, was added drop by drop to a solution of 50 g of stannous chloride in 60 ml of concentrated hydrochloric acid, at 40-60° with constant stirring. After all the nitroso-compound had been added the flask was placed on a boiling water-bath, and stirring was continued for a further 50 min. The reaction mixture was then made alkaline with 50% caustic potash, and the dark-colored product was extracted with ether. The ether was then distilled off, and the residue was recrystallized from alcohol, giving 13.6 g of 1-p-amino-phenyl-2,5-dimethyl-4-piperidone (III) crystals, m.p. 135.5-136.5°, which rapidly darken on exposure to the atmosphere.

Found %: N 13.01; 13.03
$C_{13}H_{18}ON_2$. Calculated %: N 12.83

The hydrochloride of the dinitrophenylhydrazone was obtained by adding an alcoholic solution of 2,4-dinitrophenylhydrazine, acidified with hydrochloric acid, to an alcoholic solution of 1-p-aminophenyl-2,5-dimethyl-4-piperidone; it melts at 115-116°; after recrystallization from alcohol.

1-p-Benzylideneaminophenyl-2,5-dimethyl-4-piperidone (IV). A mixture of 2 g of 1-p-aminophenyl-2,5-dimethyl-4-piperidone (m.p. 135.5-136.5°), 5 ml of alcohol, and 2 ml of benzaldehyde was heated at 60-70° for 1 hour. The cooled solution deposited yellow crystals, recrystallization of which from absolute alcohol gave 1.9 g of 1-p-benzylideneaminophenyl-2,5-dimethyl-4-piperidone (IV), yellow crystals, m.p. 130.5-131.5°.

Found %: N 9.26; 9.32
$C_{20}H_{22}ON_2$. Calculated %: N 9.14

4-(2,5-dimethyl-4-ketopiperidino)-azobenzene-4'-sulfonic acid (V). A solution of 5 g of sodium sulfanilate and 2 g of sodium nitrite in 20 ml of water was added to a mixture of 12 ml of concentrated hydrochloric acid and 50 g of crushed ice, and the resulting solution of diazobenzenesulfonic acid was cooled to −4°, and added drop by drop, with stirring, to a solution of 5 g of 1-phenyl-2,5-dimethyl-4-piperidone (b.p. 116-118° at 1 mm; n_D^{20} 1.5521) in 6 ml of hydrochloric acid (1:1).

The solution was made alkaline with dilute caustic soda, when a brown precipitate of the azo-dye (V) separated. It was collected and washed on the filter with water; yield 6.5 g of sodium 4-(2,5-dimethyl-4-keto-piperidino)-azobenzene-4'-sulfonate (V), a brown powder, dilute solutions of which are colored yellow, changing to an intense red when acidified.

Found %: N 10.13; 10.35
$C_{19}H_{20}O_4N_3SNa$. Calculated %: N 10.26

4-Amino-1-phenyl-2,5-dimethylpiperidine (VII). a) Preparation of the oxime of 1-phenyl-2,5-dimethyl-4-piperidone (VI). A solution of 30 g of 1-phenyl-2,5-dimethyl-4-piperidone (b.p. 117-118° at 1 mm, n_D^{20} 1.5519) in 150 ml of alcohol was mixed with a solution of 30 g of hydroxylamine hydrochloride and 60 g of sodium acetate in 100 ml of water, and the resulting suspension was heated for a short time on a water-bath. The cooled solution was filtered, and the residue was dried in a vacuum desiccator, giving 31 g of the oxime of 1-phenyl-2,5-dimethyl-4-piperidone (VI), which melted at 70-83° after two recrystallizations from 50% alcohol.

Found %: N 12.80; 13.14
$C_{13}H_{18}ON_2$. Calculated %: N 12.83

b) Reduction of the oxime of 1-phenyl-2,5-dimethyl-4-piperidone (VI). A solution of 25 g of oxime in 300 ml of isoamyl alcohol was placed in a flask fitted with a stirrer and a reflux condenser, and 24 g of sodium was added gradually, avoiding violent boiling of the system. The flask is then heated until all the sodium has dissolved, and the solution was then cooled, 250 ml of water and 400 ml of ether were added, the ethereal extract was washed with 100 ml of water, and dried with sodium sulfate. The ether and the isoamyl alcohol were then distilled off, and the residue was vacuum distilled, giving 18 g of 4-amino-1-phenyl-2,5-dimethylpiperidine (VII), a colorless liquid with a powerful odor of amine, b.p. 114-115° at 1 mm, n_D^{20} 1.5425; d_4^{20} 1.0035; found MR_D 64.11; calculated MR_D 63.96.

Found %: N 13.78; 13.73
$C_{13}H_{20}N_2$. Calculated %: N 13.71

The amine thus obtained readily absorbs atmospheric carbon dioxide, giving a carbonate, m.p. above 100°.

4-Amino-1-phenyl-2,5-dimethylpiperidine dihydrochloride was obtained by passing dry hydrogen chloride into a solution of the amine in ether-alcohol mixture. It melted at 204-206°, after recrystallization from absolute alcohol.

Found %: Cl 25.11
$C_{13}H_{22}N_2Cl_2$. Calculated %: Cl 25.60

4-Acetamido-1-phenyl-2,5-dimethylpiperidine (VIII). 2 g of 4-amino-1-phenyl-2,5-dimethylpiperidine (b.p. 114-115° at 1 mm, n_D^{20} 1.5425) was mixed with 2.5 g of acetic anhydride, and the mixture was heated on the water-bath for 30 min., after which it was made alkaline with 20% potassium hydroxide solution. The crystalline precipitate was washed with water; yield, 2.2 g of 4-acetamido-1-phenyl-2,5-dimethylpiperidine (VIII), m.p. 146-148° (from alcohol-gasoline mixture).

Found %: N 11.33; 11.26
$C_{15}H_{22}ON_2$. Calculated %: N 11.37

4-Methylamino-1-phenyl-2,5-dimethylpiperidine (X). 9 g of 1-phenyl-2,5-dimethyl-4-piperidone (b.p. 116-118° at 1 mm, n_D^{20} 1.5519) was placed in a glass tube immersed in a freezing mixture, and dry methylamine was passed until the weight had increased by 11.5 g, when the tube was sealed and heated for 3 hrs at 65°. The excess of methylamine was removed under reduced pressure, and the residue was dissolved in 30 ml of absolute alcohol. The solution of 4-methylimino-1-phenyl-2,5-dimethylpiperidine (IX) was hydrogenated (Pt catalyst; Adams method); 730 ml of hydrogen (18° at 758 mm). 6.5 g of a colorless, viscous liquid with a characteristic odor of amine was obtained, b.p. 119-121° at 1 mm, n_D^{20} 1.5522, and its ethereal solution was saturated with dry hydrogen chloride, giving a colorless hygroscopic hydrochloride, which was purified by dissolving in acetone and precipitating out with ether, giving 3.1 g of 4-methylamino-1-phenyl-2,5-dimethylpiperidine dihydrochloride (X); m.p. 195.5-197° (in a sealed capillary), as small crystals, readily soluble in water.

Found %: N 9.39; 9.51; 9.32; Cl 24.06
$C_{14}H_{24}N_2Cl_2$. Calculated %: N 9.61; Cl 24.37

1-Cyclohexyl-2,5-dimethyl-4-piperidol (XI). 46 g of 1-phenyl-2,5-dimethyl-4-piperidone (b.p. 115-116° at 0.8 mm, n_D^{20} 1.5521) in 53 ml of alcohol was hydrogenated (0.6 g of Raney Ni) in a rotating autoclave of capacity 156 ml, at 200-250° and an initial hydrogen pressure of 90 atm. Altogether 4.33 moles of hydrogen were absorbed per mole of piperidone. The solution was filtered, to remove catalyst, and the hydrogenation product was fractionally distilled in vacuum, giving the following fractions:

Fraction I, b.p. 70-100° at 10 mm; 24 g
Fraction II, b.p. 115-125° at 1 mm; 13 g

An ethereal solution of Fraction II (b.p. 115-125° at 1 mm) was saturated with hydrogen chloride, to give a hydrochloride which, after two recrystallizations from alcohol, melted at 305-307°, and which when treated with 25% aqueous ammonia yielded the free base, m.p. 85-86° (from gasoline). The base and its hydrochloride gave no m.p. depression when mixed with 1-cyclohexyl-2,5-dimethyl-4-piperidol (XI) or its hydrochloride, previously prepared in our laboratory from 2,5-dimethyl-4-piperidone (m.p. 98°), formic acid, and cyclohexanone.

An ethereal solution of Fraction I (b.p. 70-100° at 10 mm) was saturated with hydrogen chloride, and the ethereal layer was carefully decanted off. The residue after the ether had been distilled off, consisting of neutral products, was three times distilled at atmospheric pressure, giving 2.1 g of substance of b.p. 140-143°, n_D^{20} 1.4190 (the literature [4] gives for 2-methylhexan-3-ol (XII) a b.p. of 141-142°, n_D 1.41493). The product (1.5 g) was shaken for 1 hr with a solution of 1.2 g of potassium dichromate in 30% sulfuric acid, and the oxidation product was extracted with ether. Its semicarbazone melted at 116-118° (from 50% alcohol), and gave no depression of m.p. with the semicarbazone, m.p. 117-119°, of a known sample of 2-methyl-hexan-3-one (XIII) [5].

SUMMARY

A series of transformations of 1-phenyl-2,5-dimethyl-4-piperidone (I) affecting the keto group and the phenyl radical are described. The compounds II - XI have not previously been described.

Received April 15, 1952

Institute of Organic Chemistry
Academy of Sciences USSR

LITERATURE CITED

[1] I. N. Nazarov, S. G. Matsoyan, and V. A. Rudenko, Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 6, 1057 (1952). (See Consultants Bureau English Trasnlation, p. 923.)

[2] J. R. Thayer, S. M. McElvain, J. Am. Chem. Soc., 49, 2862 (1927); N. W. Bolyard, J. Am. Chem. Soc., 52, 1030 (1930).

[3] Ch. Mayer, Bull. (3) 31, 140, 953 (1904).

[4] J. Muset, Bull. Acad. Roy. Belgique 775 (1906); C. 1907, I, 1313.

[5] H. Meerwein, Ann., 419, 138 (1919).

BLANK
PAGE

CATALYTIC HYDROCONDENSATION OF CARBON MONOXIDE WITH OLEFINS

PART 9. REACTION OF METHANOL AND ETHANOL WITH ETHYLENE

Ya. T. Eidus and I. V. Guseva

It has been shown earlier [1,2,3] that a mixture of ethylene and hydrogen does not react under the ordinary conditions of catalytic hydrocondensation unless the mixture contains some carbon monoxide, even very small admixtures being effective in this respect. The effect increases as the carbon monoxide content of the mixtures rises from 0 to 6%, as is shown by rise in the yield of hydrocarbons, in particular of the heavier fractions. It was suggested that the methylene radicals formed at the catalyst surface by hydrogenation of carbon monoxide may act as initiators of the reaction, and may at the same time enter into the composition of the newly formed hydrocarbon molecules, as is shown by the presence among the reaction products of hydrocarbons with an odd number of carbon atoms in the molecule.

It was natural to expect that the same condensing action on ethylene (olefin) hydrogen mixtures would be exerted by such substances which would not under the given conditions act as contact catalyst poisons, but would decompose to yield either methylene radicals (for example, ketene [4] or perhaps diazomethane) or carbon monoxide, which could undergo hydrogenation at the catalyst surface to yield methylene radicals.

We first examined methanol as being a substance whose chemical structure is such as would lead us to expect it to exert a condensing effect in the reaction with ethylene, since it is known that methanol readily decomposes at various contact catalysts with liberation of carbon monoxide, by the reaction:

$$CH_3OH \longrightarrow (HCHO + H_2) \longrightarrow CO + 2H_2 \qquad (1)$$

Moreover, since the second product of reaction (1) is hydrogen, the presence of which is necessary for the reaction of hydrocondensation of carbon monoxide with olefins, it could have been supposed that it would under the given conditions be possible [1,2] to realize the reaction of hydrocondensation of methanol with the simpler olefins, according to the scheme:

$$CH_3OH + CH_2 = CH_2 \longrightarrow (CO + 2H_2 + C_2H_2 = CH_2) \longrightarrow (CH_2 + H_2O + CH_2 = CH_2) \longrightarrow CH_3CH = CH_2 + H_2O;$$

$$CH_3OH + CH_3CH = CH_2 \longrightarrow (CO + 2H_2 + CH_3CH = CH_2) \longrightarrow (CH_2 + H_2O + CH_3CH = CH_2) \longrightarrow$$

$$\longrightarrow CH_3CH_2CH = CH_2 + H_2O \text{ etc.} \qquad (2)$$

The same reasoning would apply to ethanol, under such conditions [5] of catalyzed decomposition as in the reaction:

$$CH_3CH_2OH \longrightarrow (CH_3CHO + H_2) \longrightarrow CO + H_2 + CH_4. \qquad (3)$$

i.e., with formation of carbon monoxide and hydrogen.

Hydrocondensation of ethylene with ethanol would accordingly proceed as follows:

$$CH_3CH_2OH + CH_2 = CH_2 + H_2 \longrightarrow (CO + 2H_2 + CH_2 = CH_2 + CH_4) \longrightarrow (CH_2 + H_2O + CH_2 = CH_2 + CH_4) \longrightarrow$$

$$\longrightarrow CH_3CH = CH_2 + H_2O + CH_4; \qquad CH_3CH = CH_2 + CH_3CH_2OH + H_2 \longrightarrow (CO + 2H_2 + CH_3CH = CH_2 + CH_4 \longrightarrow$$

$$\longrightarrow (CH_2 + H_2O + CH_3CH = CH_2 + CH_4) \longrightarrow CH_3CH_2CH = CH_2 + H_2O + CH_4. \qquad (4)$$

The results of the present research do in fact show that both methanol and ethanol exert a condensing effect on ethylene-hydrogen mixtures, as well as entering into reaction with ethylene to yield final reaction products. In view of the common features of the mechanism of hydrocondensation of carbon monoxide with ethylene and of methanol or ethanol with ethylene, we must accept the intermediate formation from the alcohols of carbon monoxide and hydrogen, and subsequently of methylene radicals, i.e., we must admit the correctness of the reaction schemes (3) and (4).

EXPERIMENTAL

The apparatus, the preparation and analysis of the initial and final gases, and the experimental methods applied, were the same as in our earlier papers [1,2]. The methanol used boiled at 64.4-64.6° at 755 mm, d_4^{20} 0.7918; n_D^{20} 1.3291 (99.8% methanol [6]), and the ethanol had b.p. 77.9-78.1° at 755 mm, d_4^{20} 0.8086; n_D^{20} 1.3630 (93.7% ethanol [6]). The initial ethylene-hydrogen mixture was passed at a constant speed through a vertical graduated tube filled with methanol or ethanol, before entering the catalysis tube. It was thus possible for each experiment to measure the amount of alcohol carried along with the stream of gas into the reaction space. Unreacted alcohol condensed together with reaction products in the receiver at room temperature and in that cooled at −80°, where it was found in the aqueous alcoholic layer. The amount of alcohol which had entered into the reaction was taken as the difference between the amount passed and that recovered.

For experiments with methanol the amount of unreacted alcohol was derived from the density [6] and the amount of the aqueous alcoholic layer of reaction products, which contained only insignificant admixtures of other oxygen-containing substances which could affect the accuracy of this determination. In the case of ethanol this layer contained up to 2.5 v/v-% of acids (counted as acetic acid), as was shown by direct titration with 0.1 N caustic soda solution, as well as up to 4.2% of aldehydes (counted as acetaldehyde). The aldehyde content was determined by adding hydroxylamine hydrochloride and titrating the hydrochloric acid liberated in the reaction of oxime formation. In view of the presence of these admixtures the determination of the amount of unreacted alcohol was effected as follows. The acids in the aqueous alcoholic layer were exactly neutralized by adding the appropriate amount of alkali, and the aldehyde was bound by boiling the neutral solution for 5 hrs under reflux with freshly precipitated mercuric oxide (prepared from equimolecular amounts of mercuric chloride and sodium hydroxide [7]). The solution was then distilled until all the alcohol had passed over, and the alcohol content of the distillate was derived from its density [6].

1. Hydrocondensation of methanol with ethylene

The results of the experiments with methanol and ethylene are given in Tables 1-4.

The experiments were conducted at 200°, using five specimens of catalyst (contacts 37, 38, 39, 40 and 41) in about 15 g portions in layers 40-45 cm long, in a glass tube 10 mm in diameter. Contacts 37, 38, and 39 were taken for the reaction after having previously been used in experiments on hydrocondensation of carbon monoxide with ethylene, involving mixtures of ethylene and hydrogen containing 5% of carbon monoxide (experiments 191, 193, and 196). Contacts 40 and 41 were taken freshly prepared for the reactions of hydrocondensation of methanol with ethylene.

Table 1 presents for each experiment its duration in hours, the percentage composition of the initial and final gases, the flow velocity of the initial gas in liters per liter of catalyst per hour (l/l/hr) the amount of pure methanol passed, in grams, and its flow velocity in l/l/hr (referring to the liquid alcohol).

Table 2 gives the percentage composition of the "theoretical initial gas". It is assumed that hydrocondensation of methanol with ethylene proceeds according to scheme (2), i.e., with previous decomposition of methanol according to reaction (1), to yield carbon monoxide and hydrogen. For this reason the "theoretical initial gas" consists of the initial gas ($C_2H_4 + H_2$) and of the gas ($CO + H_2$) which should be formed by the total decomposition of all the reacted methanol according to reaction (1). Table 2 also gives the percentages of methanol entering into the reaction, as well as, for a number of experiments, of ethylene, hydrogen, and carbon monoxide entering into the composition of the "theoretical initial gas" (as percentages of the initial component). The fraction of ethylene which had undergone conversion into ethane is also given in this Table.

Table 3 gives the yields of heavy oil, light oil, and Gasol (C_3 and C_4), and the total yield of condensate (not counting the aqueous layer), in ml per m^3 of "theoretical initial gas". The molecular proportions of methanol, hydrogen, and ethylene entering into the hydrocondensation reaction are given for some of the experiments. It is evident that the part of the reacted methanol which entered into the hydrocondensation reaction is expressed by the fraction of reacted carbon monoxide in the "theoretical initial gas", inasmuch as the actual initial gas did not contain any carbon monoxide. The amount of carbon monoxide in the final gas represents that part of the methanol which had decomposed according to reaction (1), but had not entered into reaction (2). The fractions of reacted ethylene which had entered into the hydrocondensation reaction can be derived by subtracting from the total amount of ethylene or hydrogen which had entered into the overall reaction that part which had been used in the hydrogenation reaction with formation of ethane.

TABLE 1

Catalyst No.	Expt. No.	Duration of expt. in hrs.	Composition of the initial gas, %			Volume velocity 1/1/hr	Composition of final gas, %				Methanol introduced g	Volume velocity of methanol 1/1/hr
			C_2H_4	H_2	CO		C_2H_4	H_2	CO	C_2H_6		
37	191	10	54.8	40.1	5.1	91	8.4	10.9	1.1	79.6	–	–
	192	20	57.2	42.8	0.0	68	4.0	26.5	3.1	66.4	5.26	0.01
38	193	5.5	56.1	38.9	4.8	72	1.0	40.6	0.0	58.4	–	–
	194	16	72.7	26.6	0.7	60	–	–	–	–	6.49	0.01
	195	15	68.0	32.0	0.0	54	31.1	17.9	5.5	45.5	8.01	0.02
39	196	20	63.5	31.3	5.2	70	–	–	–	–	–	–
	197	11	68.2	31.8	0.0	51	–	–	–	–	5.04	0.015
	198	11.5	70.3	29.7	0.0	58	26.7	12.6	5.6	55.1	4.91	0.01
40	199	36.0	62.3	37.7	0.0	64	15.4	14.0	5.0	65.6	15.20	0.015
41	200	16.7	60.4	39.6	0.0	67	6.5	21.3	4.7	67.5	6.41	0.01
	201	10.0	61.8	38.2	0.0	62	5.9	16.1	6.5	71.5	4.47	0.02
	202	15.0	70.7	29.3	0.0	58	–	–	–	–	6.85	0.02

TABLE 2

Expt. No.	Composition of "theoretical initial gas", %				Reacted, %			Yield of C_2H_6 as % reacted C_2H_4	% by wt. of methanol reacted
	C_2H_4	H_2	CO	Volume velocity 1/1/hr	C_2H_4	H_2	CO		
191	–	–	–	–	95.5	92.7	94.2	44.2	–
192	47.6	46.7	5.7	81	97.2	81.3	81.8	47.6	77.6
193	–	–	–	–	99.5	73.0	100.0	27.0	69.5
194	57.3	35.0	7.7	76	–	–	–	–	–
195	50.8	40.8	8.4	73	69.1	77.9	66.9	65.0	60.9
196	–	–	–	–	–	–	–	–	–
197	50.1	41.1	8.8	69	–	–	–	–	72.6
198	56.6	36.9	6.5	72	81.2	86.4	65.5	47.9	59.9
199	47.5	44.7	7.8	84	88.0	88.4	76.7	58.0	80.6
200	46.0	46.1	7.9	89	97.0	91.0	93.1	22.2	92.0
201	46.5	45.3	8.2	82	95.6	86.3	87.8	55.2	76.1
202	55.3	37.5	7.2	74	–	–	–	–	59.1

As is evident from Tables 1-3 hydrocondensation of methanol with ethylene proceeds at the fresh catalyst surface (contacts 40 and 41, experiments 199-202) as well as at surfaces which have previously been used in experiments with carbon monoxide (contacts 37,38, and 39, experiments 192, 194, 195, 197, and 198). When the methanol entered the reaction tube with a volume velocity of 0.01-0.02 60-90% of it took part in the overall reaction. As is shown by the fraction of reacted carbon monoxide in the "theoretical initial gas", from 68 to 100% of the methanol entering into the reaction undergoes hydrocondensation with ethylene, and 0-32% remains in the final gas as carbon monoxide, formed by reaction (1). A "theoretical initial gas" being delivered with a volume velocity of 70-90 contained 46-57% of ethylene, 35-47% of hydrogen, and 5.7-8.8% of carbon monoxide. Of the ethylene 69-99.5% entered into reaction, and from 22 to 65% of the reacted ethylene underwent hydrogenation to give ethane. The molar ratios of methanol, hydrogen, and ethylene entering into the hydrocondensation reaction were on the average as 1:3:5, and these ratios are close to the corresponding ones for the reaction of hydrocondensation of carbon monoxide with ethylene (compare experiments 191 and 192). The total yield of condensate (not counting reaction water and unreacted alcohol) was 300-500 ml per m^3 of "theoretical initial gas", or 25-30 ml /1/hr., which is also

TABLE 3

Expt. No.	Yield, ml/m³		Yield (t + l + g)			Molecular proportions of CO (or CH_3OH) entering into the hydrocondensation reaction: $H_2:C_2H_4$
	Heavy oil, (t)	Light oil (l)	Gasol (g)	ml/m³	ml/1/hr	
191	132.0	164.7	239.3	536.0	44.3	1:3.3:5.7
192	7.9	122.8	154.6	285.3	23.2	1:3.2:5.2
193	112.2	165.3	284.3	561.8	36.9	–
194	51.2	122.5	189.3	363.0	27.5	–
195	19.8	81.6	64.3	165.7	12.1	–
196	89.6	156.7	164.2	410.2	29.0	–
197	58.9	162.8	297.8	519.5	35.9	–
198	22.1	88.7	237.5	348.3	25.1	1:2.4:5.3
199	44.1	102.4	209.0	355.5	30.0	1:2.5:3.0
200	50.2	104.4	172.0	326.6	29.0	–
201	31.2	83.3	267.5	382.0	31.5	–
202	23.4	106.0	248.3	377.7	27.8	–

TABLE 4

Fraction	Yield % by vol.	d_4^{20}	n_D^{20}	Bromine number	% of unsaturated hydrocarbons
B.p. below 150°	67.2	0.6893	1.3925	107	67
B.p. 150-220°	15.5	0.7532	1.4245	47	48
Residue	17.3	0.8043	1.4205	19	–

close to the yields of condensate obtained by hydrocondensation of carbon monoxide with ethylene, at corresponding concentrations of carbon monoxide in the initial gas. These results show that the reaction does actually proceed according to equation (2). Some of the properties of the individual fractions of the oily products of hydrocondensation of methanol with ethylene are given in Table 4. They are closely similar to the properties of the corresponding products of hydrocondensation of carbon monoxide with ethylene.

TABLE 5

Catalyst	Expt. No.	Duration of expt. in hr.	Composition of the initial gas,%				Comp. of final gas, in %				Ethanol introduced, g	Volume velocity of ethanol 1/1/hr
			C_2H_4	H_2	CO	Volume velocity 1/1/hr	C_2H_4	H_2	CO	C_nH_{2n+2}		
44	213	15	44.2	55.8	0.0	103	2.0	37.9	2.2	57.9	26.4	0.11
	214	15	46.1	53.9	0.0	108	1.1	36.8	1.1	61.0	19.4	0.06
	215	15	57.2	42.8	0.0	112	12.5	19.7	3.1	64.7	16.8	0.07
45	216	10	58.7	41.3	0.0	62	4.5	17.1	2.0•	73.7	12.0	0.04
	217	5	50.9	49.1	0.0	59	4.5	14.9	1.5••	77.6	6.8	0.05

• The final gas of experiment 216 also contained 2.7% CO_2.

•• The final gas of experiment 217 also contained 1.5% CO_2.

2. Hydrocondensation of ethanol with ethylene

The results of experiments on the hydrocondensation of ethanol with ethylene are given in Tables 5-7.

The experiments were conducted as for methanol, at 200°. Two specimens of catalyst were taken (contacts 44 and 45); the experiments were done with previously unused catalysts. The data of Tables 5,6, and 7 correspond to those of Tables 1, 2 and 3 for methanol.

TABLE 6

No. of experiment	Composition of "theoretical initial gas", %					Reacted, in %			Yield of C_2H_6 as % of reacted C_2H_4	% by weight of ethanol reacted
	C_2H_4	H_2	CO	CH_4	Volume velocity 1/1/hr.	C_2H_4	H_2	CO		
213	24.8	46.0	14.6	14.6	183	97.3	72.5	93.7	18.2	72.6
214	29.9	46.7	11.7	11.7	166	98.6	73.0	96.9	31.5	70.9
215	42.4	40.4	8.6	8.6	151	90.5	84.1	88.3	32.4	58.3
216	39.2	38.6	11.1	11.1	93	96.4	85.3	94.8	32.3	71.6
217	32.6	43.4	12.0	12.0	94	94.8	86.8	95.2	57.0	69.0

TABLE 7

No. of experiment	Yield, ml/m³			Yield (t + l + g)	
	Heavy oil (t)	Light oil (l)	Gasol (g)	ml/m³	ml/l/hr.
213	11.7	87.4	128.1	227.2	35.4
214	6.2	68.2	161.2	235.6	34.5
215	0.0	37.4	209.0	246.4	34.0
216	28.7	121.4	115.0	265.1	22.0
217	26.0	104.0	78.0	208.0	17.0

TABLE 8

Fraction	Yield % by vol.	d_4^{20}	n_D^{20}	Bromine number	% of unsaturated hydrocarbons
b.p. below 150°	80	0.7124	1.3830	55	38
b.p. 150-210°	11.6	0.7559	1.4239	36	30
Residue, b.p. above 210°	4.2	–	–	–	–

We assume that the hydrocondensation of ethanol with ethylene proceeds according to scheme (4), i.e., with preliminary decomposition of ethanol according to reaction (3), giving carbon monoxide, hydrogen, and methane. For this reason the "theoretical initial gas" consists of the initial gas ($C_2H_4 + H_2$) and of the gas which should be formed as a result of reaction (3) from that amount of ethanol represented by the difference between alcohol introduced and alcohol recovered unchanged or as acetaldehyde and acetic acid. The yields of condensate given in Table 7 are calculated on "theoretical initial gas" taken, the volume of methane formed being subtracted.

The data of Tables 5-7 show that hydrocondensation of ethanol with ethylene takes place. 58.3-72.6% of the ethanol entering the reaction zone with a flow velocity of 0.04-0.11 entered into reaction. As is shown by the ratio of reacted carbon monoxide in the "theoretical initial gas", 88-97% of the ethanol which enters into reaction takes part in the hydrocondensation reaction, and only 3-12% of it remains in the final gas as carbon monoxide, which may have been formed by reaction (3). As appears from Table 6, the "theoretical initial gas" had the composition: ethylene 25-42, hydrogen 39-47, carbon monoxide 9-15, and methane 9-15%. 90-99% of the ethylene entered into reaction, and 18-57% of this amount was hydrogenated to ethane. The total yield of condensate (not counting the aqueous alcoholic layer) was 208-246 ml per m³ of "theoretical initial gas" (subtracting methane), or 17-35 ml/l/hr.

Some of the properties of the individual oily fractions of the product of hydrocondensation of ethanol with ethylene are given in Table 8. The somewhat high values found for the density, and the low values for the refractive index of the fraction of b.p. below 150° are due to presence of oxygen-containing products, as is confirmed by boiling the fraction with sodium for 3 hours, after which the density becomes 0.7066, and the refractive index 1.3862.

SUMMARY

1. Similarly to carbon monoxide, methanol and ethanol promote the reaction of condensation of ethylene and hydrogen, and at the same time enter into the hydrocondensation reaction with ethylene.

2. The total yield of condensate (not counting water and unreacted alcohol) amounts to 17-35 ml per liter of catalyst per hour.

3. The experimental results confirm the view that the process involves the preliminary decomposition

of the alcohols, with production of carbon monoxide and hydrogen, which then, through the intermediate stage of formation of methylene radicals, enter as usual into the reaction of hydrocondensation with ethylene.

LITERATURE CITED

[1] Ya. T. Eidus, N.D. Zelinsky, and K.V. Puzitsky. Bull. Acad. Sci., Div. Chem. Sci., No. 1, 110, 326 (1949).

[2] Ya. T. Eidus, N.D. Zelinsky, and N. I. Ershov, Doklady 60, 599 (1948).

[3] N.D. Zelinsky, ibid., 60, 235 (1948).

[4] B.R. Warner, M.J. Derrig, C. W. Montgomery, J. Am. Chem. Soc., 68, 1615 (1946).

[5] V.A. Plotnikov, et al Acta Phys. Chem., U.R.S.S. 1, 493 (1934). A.V. Frost, ibid., 511; Ya. T. Eidus. Bull. Acad. Sci. U.S S R, Div. Chem. Sci., No. 1, 65, (1943); P.K. Frolich, M.R Fenske et al, Ind Eng. Chem. 20, 694, 1327 (1928), 21, 109, 867, 1052 (1929); G.F. Huttig, O. Kostelitz et al, Z. Allg. anorg. Chem. 197, 129 (1931); Koll.- Z 67, 965 (1934).

[6] A.G. Doroshevsky. Researches on aqueous alcoholic solutions, 114 (1911).

[7] G. Gorr, I. Wagner, Biochem. Z. 161, 489 (1925).

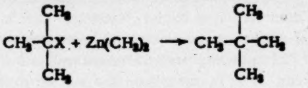
Received March 7, 1952

Institute of Organic Chemistry
Academy of Sciences U.S.S.R

SYNTHESIS AND PROPERTIES OF TETRAPROPYLMETHANE, TETRABUTYLMETHANE, AND TETRAHEXYLSILANE

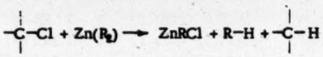
A. D. Petrov and E. A. Chernyshev

The tetraalkylmethane series has been insufficiently studied. Its first member, tetramethylmethane, was obtained by Lvov [1] in 1870, by the reaction: *



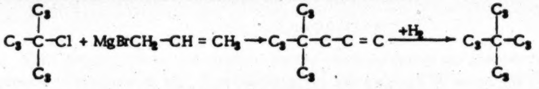
$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}X + Zn(CH_3)_2 \rightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$$

This hydrocarbon was next prepared by a Grignard synthesis [2], but Morgan [3] was unable to prepare the second member, tetraethylmethane, by this method, and had to use Lvov's method for the purpose. Karrer and Ferri [4] attempted to prepare tetra-n-butylmethane by this same method, notwithstanding that Vagner [5] and Pavlov [6] had pointed out the tendency of the higher zinc alkyls to decompose with formation of olefinic hydrocarbons and with reduction of the tertiary chloride by the reaction:

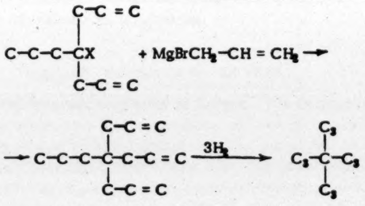


$$-\overset{|}{\underset{|}{C}}-Cl + Zn(R_2) \rightarrow ZnRCl + R-H + -\overset{|}{\underset{|}{C}}-H$$

As we showed in our preceding paper [7], Karrer and Ferri actually obtained tributylmethane, which they mistakenly identified as tetrabutylmethane. In the same paper we described the synthesis of tetrapropylmethane by reactions (1) and (2):



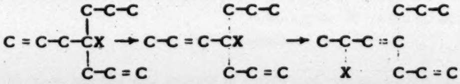
$$C_3-\overset{C_3}{\underset{C_3}{C}}-Cl + MgBrCH_2-CH=CH_2 \rightarrow C_3-\overset{C_3}{\underset{C_3}{C}}-C-C=C \xrightarrow{+H_2} C_3-\overset{C_3}{\underset{C_3}{C}}-C_3 \quad (1)$$



$$C-C-C-\overset{C-C=C}{\underset{C-C=C}{C}}X + MgBrCH_2-CH=CH_2 \rightarrow C-C-C-\overset{C-C=C}{\underset{C-C=C}{C}}-C-C=C \xrightarrow{3H_2} C_3-\overset{C_3}{\underset{C_3}{C}}-C_3 \quad (2)$$

The yield obtained by reaction (1) was 10%, and by reaction (2) 30%.

The mixture of products obtained by reactions (1) and (2) was subjected to hydrogenation. The hydrogenation product was distinguished by its very low freezing point, which led us to suspect that tetrapropylmethane is obtained only by reaction (1), and that in reaction (2) a hitherto unknown reaction of isomerization of the alkyl halide with double bonds in the γ-position takes place, analogous to the allyl rearrangement:



$$C=C-C-\overset{C-C-C}{\underset{C-C=C}{C}}X \rightarrow C-C=C-\overset{C-C-C}{\underset{C-C=C}{C}}X \rightarrow C-\underset{X}{C}-C=\overset{C-C-C}{\underset{C-C=C}{C}}$$

In this research we repeated reaction (2), and by oxidation of the product of synthesis (α-methylvaleric acid and methyl propyl ketone were isolated and identified) we showed that this assumption was correct, and that hydrogenation of the product of reaction (2) gives 4-methyl-6-propylnonane, not tetrapropylmethane.

In view of the low yield of tetrapropylmethane by reaction (1) we investigated the reaction of condensation with C_3MgX, with a saturated alkyl halide (a) at elevated temperatures and (b) in presence of the condensing agent $HgCl_2$. We applied these findings to the synthesis of tetrabutylmethane, which has not previously been described. We were not, however, able to obtain tetrahexylmethane, partly because of the instability of the halohydrin of trihexylcarbinol, and partly because with increase in the length of the radical R of MgRX a form of decomposition analogous to that found for zinc propyl or butyl takes place. As a result we obtained only trihexylmethyl chloride and the olefin produced by elimination of HCl from it.

We then, bearing in mind Whitmore's remark, that "the synthesis of readily available silanes with quaternary silicon atoms may serve in place of their much more difficultly preparable carbon analogs for the elucidation of the properties of such structures", turned to the synthesis of tetrahexyl- and tetraoctylsilane. We here bore in mind the closeness of the boiling points and the densities, but not the freezing points, since Bygden [9] has shown that hexamethyldisilane freezes at 12°, while the f.p. of its carbon analog is at 100°. The physical constants of the hydrocarbons prepared by us, and of their structural analog tetrahexylsilane, are given in Table 1.

TABLE 1

Physical constants of some tetraalkylmethanes and silanes

Compound	Freezing point	Boiling point	Pressure mm	n_D^{20}	d_4^{20}
Tetrapropylmethane	−26	60-62	6	1.4322	0.7706
Tetrabutylmethane	− 6	103-104	6	1.4440	0.7935
Tetrahexylsilane	−30	178-179	5	1.4532	0.8144

We were able by the action of $C_6H_{13}MgBr$ on $SiCl_4$ to obtain only $(C_6H_{13})_3SiCl$. tetrahexylsilane was prepared by heating $SiCl_4$ with LiC_6H_{13} at 90°. Tetraoctylsilane could not be obtained by the latter method, the product being $(C_8H_{17})_3SiCl$. Thus LiC_8H_{17} differs from LiC_6H_{13} when heated at 90° with $SiCl_4$ in that only three of the chlorine atoms are replaced, evidently owing to the considerable steric hindrance developed by the larger radical.

EXPERIMENTAL

1. Tetrapropylmethane was obtained by the condensation of the chlorohydrin of tripropylcarbinol with propyl bromide in presence of Mg. The chlorohydrin was prepared by saturating the carbinol with dry HCl at 0°; yield 63%. 2,2-Dipropylbutyl chloride has not previously been described; it boiled at 54-56°/7 mm, n_D^{20} 1.4378; d_4^{20} 0.8676; found MR_D 53.38; calculated MR_D 53.24.

Found %: Cl 19.58; 19.67

$C_{10}H_{21}Cl$. Calculated %: Cl 19.85

The condensation reaction was conducted as follows. The Grignard reagent was prepared in the usual way from 95 g of propyl bromide, 18.5 g of magnesium, and 200 ml of absolute ether. 3.5 g of mercuric chloride was added, followed by 68 g of tripropylmethyl chloride, added drop by drop during 8 hours at 20-25°, and the reaction mixture was left over night, after which it was boiled for 2 hours, and treated with 10% HCl. The ethereal layer was dried with Na_2SO_4, and the ether was distilled off on a water-bath. The residue was fractionally distilled in vacuo, giving two fractions: Fraction I, 34.5 g, b.p. 33-35°/6 mm, n_D^{20} 1.4374, d_4^{20} 0.7682, was 4-propylhept-3-ene, produced by elimination of HCl from the chloride; published constants [10] are b.p. 160-162°/734 mm, n_D^{20} 1.4386.

Fraction II (12.0 g), b.p. 60-62°/6 mm, was tetrapropylmethane. It was treated with concentrated H_2SO_4, water, sodium carbonate solution, dried, boiled with Na, and redistilled, giving 9.2 g, b.p. 60-61°/6 mm., n_D^{20} 1.4322, d_4^{20} 0.7706, m.p. -26.5°, calculated MR_D 62.23, found MR_D 62.07, yield 12.7%.

Found %: C 84.30; 84.30; H 15.30; 15.10

$(C_3H_7)_4C$ Calculated %: C 84.66 H 15.34

The same method was applied in a different variant, as follows. The ether was distilled off from the Grignard compound, an equivalent amount of isooctane was added, followed by tripropylmethyl chloride at 80-90°; the yield of tetrapropylmethane was 11.5%. Altogether, 15 g of tetrapropylmethane was prepared.

2. Tetrabutylmethane. Tributylmethyl chloride was prepared by saturating the carbinol with HCl at 0° (70% yield). It has not previously been prepared; its constants are: b.p. 102-103°/7 mm, n_D^{20} 1.4465, d_4^{20} 0.8744, found MR_D 66.70, calculated MR_D 67.09.

Found %: Cl 16.23; 16.08
$C_{13}H_{27}Cl$ Calculated %: Cl 16.22

According to the first variant of the synthesis of tetrabutylmethane the reaction was conducted under the same conditions as for tetrapropylmethane, giving a 22.4% yield. When the reaction was conducted at higher temperatures (80-90°), without the addition of mercuric chloride, the yield was 13-5%. According to a third variant the ether was distilled off from the Grignard compound, isooctane and 2-3 g of mercuric chloride were added, the mixture was warmed to 80-90°, and tributylmethyl chloride was gradually added, giving a 17% yield of tetrabutylmethane. Altogether 18 g of tetrabutylmethane was obtained, b.p. 103-104°/6 mm, m.p. -6°, n_D^{20} 1.4440, d_4^{20} 0.7935, found MR_D 80.48, calculated MR_D 80.68.

Found %: C 84.88; 85.03; H 15.02; 15.01
$(C_4H_9)_4C$. Calculated %: C 85.00 H 15.00

3. Attempted synthesis of tetrahexylmethane. Tri-n-hexylcarbinol and tri-n-hexylmethyl chloride were synthesized as follows: they have not previously been prepared. A mixture of 350 g of n-hexyl bromide, 170 g of ethyl oenanthate, and 350 ml of absolute ether was added drop by drop to 48 g of magnesium in 350 ml of absolute ether, at 20-30°, the mixture was left overnight, boiled for 2 hours, and poured on ice. 10% HCl was then added, and the ethereal layer was dried with Na_2SO_4. The ether was distilled off, and the residue was twice distilled, collecting the fraction of b.p. 153-154°/4.5 mm; yield 80.5 g (33%), b.p. 153-154°/4.5 mm, n_D^{20} 1.4496; d_4^{20} 0.8365; found MR_D 91.17; calculated MR_D 91.46.

Found %: C 80.11; 80.26; H 14.03; 14.29
$(C_6H_{13})_3COH$. Calculated %: C 80.28; H 14.08

Trihexylcarbinol was saturated with dry HCl at 0°, and the product was washed a few times with ice-water, and residual dissolved HCl was removed by bubbling nitrogen through it. The chloride could not be distilled, as it decomposed, with copious evolution of HCl, when heated at 70-80°/3 mm. The undistilled trihexylmethyl chloride, yield 83%, had the following properties: n_D^{20} 1.4530, d_4^{20} 0.8661. found MR_D 94.40, calculated MR_D 94.80.

Found %: Cl 10.94; 10.74
$C_{19}H_{39}Cl$: Calculated %: Cl 11.73

All further operations were performed with undistilled chloride.

Three attempts were made to synthesize tetrahexylmethane, by adding trihexylmethyl chloride to magnesium hexyl chloride in presence of small amounts of mercuric chloride at 40°, 20°, and 0°. The reaction was also attempted at 10°, in presence of 1 mole of mercuric chloride per mole of hexyl bromide, and at 65°, in absence of mercuric chloride. In all cases the sole product was 7-hexyltridec-6-ene, being the product of elimination of hydrogen chloride from trihexylmethyl chloride; not even a trace of tetrahexylmethane was formed. Attempted condensation of trihexylmethyl chloride with butyl bromide gave the same result.

7-Hexyltridec-6-ene has not previously been described. It has the following properties: b.p. 149-150°/5.5 mm, freezing point -80°, n_D^{20} 1.4490, d_4^{20} 0.7957, found MR_D 89.66, calculated MR_D 89.47.

Found %: C 85.62; 85.57; H 14.40; 14.35
$C_{19}H_{38}$. Calculated %: C 85.71; H 14.29

4. Tetrahexylsilane was prepared by the action of silicon tetrachloride on excess of hexyl-lithium. The lithium-organic compound was prepared from 216 g (1.3 moles) of hexyl bromide and 18.3 g (2.62 moles) of lithium, in ether, and 18.5 g (0.109 moles) of silicon tetrachloride was added, cooling the mixture in ice. It was then stirred for 2 hours at room temperature, the ether was distilled off, and the residue was heated at 90-100°, with stirring, for a further 5 hours, after which it was left over night. It was then treated with acid, in the usual way, and shaken with ether, the ethereal layer was washed and dried, the ether was distilled off, and the residue was washed with concentrated H_2SO_4, sodium carbonate solution and water, dried, and vacuum distilled, giving two fractions:

Fr. I, b.p. 178-179°/5.0 mm., 12 g
Fr. II, b.p. 223-225°/4.5 mm., 16.5 g

Fraction I consisted of tetrahexylsilane, b.p. 178-179°/5 mm, m.p. -30°, n_D^{20} 1.4532, d_4^{20} 0.8144, found SiR_D 7.01, yield 30%.

Found %: C 78.71; 78.74; H 13.93; 13.93; Si 7.26; 7.14
$(C_6H_{13})_4Si$. Calculated %: C 78.26 H 14.13; Si 7.60

Fraction II was hexahexyldisiloxane, b.p. 223-225°/4.5 mm, n_D^{20} 1.4547, d_4^{20} 0.8398, found SiR_D 6.9, yield 26%.

Found %: C 74.12; 74.59; H 13.45; 13.60; Si 9.75; 9.32
$C_{36}H_{78}Si_2O$. Calculated %: C 74.23; H 13.40; Si 9.62

An attempted synthesis of tetrahexylsilane from magnesium hexyl bromide and tetraethoxysilane did not give the expected product, even when the reaction mixture was boiled in paraffin solution at 170-180° for 15 hours. After the usual treatment of the reaction mixture the following two fractions were obtained:

Fr. I, b.p. 150-152°/4.5 mm
Fr. II, b.p. 223-226°/4.5 mm

Fraction I was found to consist of ethoxytrihexylsilane, yield 40%, b.p. 150-152°/4.5 mm, n_D^{20} 1.4462, d_4^{20} 0.8298, found SiR_D 7.1.

Found %: C 72.73; 73.09; H 13.61; 13 48; Si 8.14; 8.16
$C_{20}H_{44}SiO$. Calculated %: C 73.17; H 13.41 Si 8.53

Fraction II was hexahexyldisiloxane, yield 10.7%. The product obtained when tetraethoxysilane was taken instead of silicon tetrachloride was hexahexyldisiloxane, in 56% yield. Tetrahexylsilane was not obtained.

5. Attempted synthesis of tetraoctylsilane. The reaction was conducted under the same conditions, and taking the same molecular proportions of reagents as in the preparation of tetrahexylsilane through the lithium-organic compound. Although tetrahexylsilane was thus obtained in 30% yield, tetraoctylsilane was not produced at all. The final product of the reaction was found to be hexaoctyldisiloxane, in 47% yield, b.p. 320-322°/8 mm, n_D^{20} 1.4575, d_4^{20} 0.8427, found SiR_D 6.9.

Found %: C 76.37; 76.24; H 13.49; 13.51; Si 7.26; 7.30
$C_{48}H_{102}Si_2O$. Calculated %: C 76.50 H 13.60; Si 7.47

SUMMARY

1. Tetrapropylmethane and tetrabutylmethane, which have not previously been prepared, were obtained by a modified Grignard-Würtz synthesis.

2. We were not able, because of the instability of trihexylmethyl chloride, to achieve the synthesis of tetrahexylmethane under the given conditions.

3. Tetrahexylsilane, which has not previously been described, was prepared from $SiCl_4$ and LiC_6H_{13}. The analogous reaction with LiC_8H_{17} did not proceed beyond formation of $(C_8H_{17})_3SiCl$.

LITERATURE CITED

[1] M.D. Lvov. J. Russ. Phys. Chem. Soc., 2, 176 (1870); 3, 168 (1871). [2] F. Spath, Monatsh. 34, 1965 (1913); F. Whitmore, G. Fleming, J. Am. Chem. Soc. 55, 3803 (1933). [3] G. Morgan, S. Carter, A. Duck, J. Chem. Soc. 127, 1252 (1925). [4] P. Karrer, C. Ferri, Helv. chim. Acta 17, 358 (1934). [5] E. E. Vagner. Bull. Acad. des Sciences. Petersbourg, 719 (1876). [6] D.P. Pavlov. ibid, 497 (1876). [7] A.D. Petrov and E.A. Chernyshev. Doklady, 67, No. 6, 1045 (1949). [8] F Whitmore, L. Sommer et al, J. Am. Chem. Soc., 68, 475 (1946). [9] A. Bygden, Dissertat., Uppsala, 1916. [10] J M. Church, F.C. Whitmore, P.V. McGrew, J. Am. Chem. Soc. 56, 176 (1934).

Received January 4, 1952

Institute of Organic Chemistry
Academy of Sciences, U.S.S.R.

BEHAVIOR OF γ-HALOGENODIALKENYLS IN THE GRIGNARD-WÜRTZ SYNTHESIS

A. D. Petrov, M. A. Cheltsova, and E. A. Chernyshev

The literature gives only very scanty indications relating to the application in magnesium-organic syntheses of halogendialkenyls with a double bond in the α-position relative to the halogen. One of the earliest papers dealing with this problem is that of Krestinsky [1], who showed that the action of magnesium on isocrotyl bromide gave only a very small yield of Grignard reagent, large amounts of isobutylene being evolved. With acetaldehyde, magnesium isocrotyl bromide gives the appropriate secondary alcohol in 14% yield only, and with isobutyraldehyde in 15.8% yield. He also prepared the Grignard reagent from the secondary halogenoalkenyl 3-bromo-2-methylbut-2-ene, and showed that it reacted with acetaldehyde to give the desired alcohol, although he does not state in what yield. The Grignard reagent could not be obtained at all from vinyl bromide and magnesium, from which a quantitative yield of ethylene and acetylene was given. Kogerman [2] was also unable to prepare magnesium vinyl bromide. In studying the Grignard synthesis of penta-1,4-diene from allyl bromide and vinyl bromide he found that the desired diene was obtained in small yield (15%) only when magnesium-copper alloy was used. Kirrman [3] obtained the magnesium-organic compound from 1-bromohept-1-ene, in 25% yield, and by treating it with water he obtained hept-1-ene, in a yield of 20% calculated on the amount of bromide taken.

Karash and Fuchs have recently obtained a series of hydrocarbons in good yield by the reaction of vinyl bromides with magnesium phenyl and benzyl bromide in presence of the salts $CoCl_2$, $CuCl_2$, and $CrCl_3$ [4]. Without these salts, however, the reaction either did not proceed at all, or only very small yields (less than 5%) were obtained. These data provide support for the view that the presence of a double bond in the α-position to the halogen causes considerable lowering of the reactivity of alkyl halides in the Grignard synthesis.

On the other hand, the presence of a double bond in the β-position to the halogen considerably augments the reactivity of alkenyl halides; thus Levin [5] obtained a number of branched-chain olefins in yields of over 30% from 1,1,3-trimethylbutadiene hydrobromide and RMgX, whereas saturated alkyl halides of the same structure do not enter into the Grignard-Wurtz reaction at all. Young and Roberts [6] showed that primary and secondary alkenyl β-halides give even higher yields, of the order of 80-85%, in the Grignard and Grignard-Wurtz reactions. However, the use of alkenyl β-halides for the Grignard synthesis of individual hydrocarbons and alcohols is complicated by the circumstance that they tend to isomerize, with shift in the position of both the double bond and the halogen, either during distillation of the alkenyl halide, or in many cases during the actual reaction.

Only a few papers have been published on the use of alkenyl γ-halides. Schinz and Simon [7] obtained the desired alcohol in 26% yield from 5-bromo-2-methylpent-2-ene and α-methylacrolein, and they showed that the saturated bromide of the same structure gave higher yields than this. Goethals [8] obtained the magnesium-organic compound of 5-chloropent-2-ene which with acrolein gave octa-1,6-dien-3-ol, in 50% yield. The comparatively high yields of alcohols obtained in the last two cases may be due to the circumstance that primary γ-halides were taken, but chiefly because the synthesis was performed with active carbonyl compounds with a double bond in the β-position to the carbonyl group.

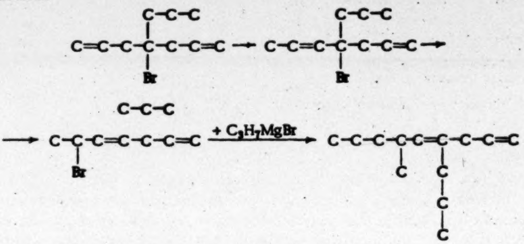
The behavior of primary, secondary, and tertiary alkenyl γ-halides in the Grignard-Würtz reaction has not yet been studied; it is the subject of the present communication.

We took 4-bromobut-1-ene, 4-bromopent-1-ene, and 4-bromo-4-methyl-pent-1-ene, and we found that these primary, secondary, and tertiary alcohols do not enter into the Grignard-Würtz reaction. 4-Bromopent-1-ene is recovered unchanged when taken for reaction with CH_3MgBr, with only a little splitting off of HBr. 4-Bromopent-1-ene similarly does not react with $CH_2{=}CH{-}CH_2MgBr$, whereas with the corresponding saturated secondary halide (taken as a Grignard reagent) and allyl bromide the product was 4-methylhept-1-ene; 4-bromo-4-methyl-help-1-ene also did not react with CH_3MgBr. The same result was obtained with 4-chloro-4-methylpent-1-ene instead of the bromide, and $Zn(CH_3)_2$ instead of CH_3MgBr. The magnesium-organic compound given by 4-bromo-4-methylpent-1-ene similarly did not react with methyl bromide, or even with so reactive an alkenyl halide as is allyl chloride. Yet CH$_3$MgBr reacted with the saturated bromide of the same structure (4-bromo-4-methylpentane), giving 2,2-dimethylpentane in 15% yield.

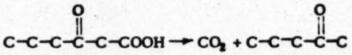
Magnesium γ-butenyl bromide did not react with tributylmethyl chloride, while magnesium butyl bromide gave tetrabutylmethane in 15% yield under the same conditions.

We have shown in an earlier paper that a condensation product is obtained from 4-bromo-4-methylhepta-1,6-diene and magnesium propyl bromide [9], and hydrogenation of the diene so obtained should be expected to yield tetrapropylmethane. However, the low reactivity of alkenyl γ-halides in Grignard-Würtz reactions, and the very low freezing point (< -70°) of the product of hydrogenation of the diene (the freezing point of tetrapropylmethane obtained by a different method is -26°), obliged us to suppose that a hitherto unknown γ-rearrangement of the unsaturated alkyl γ-halide has here taken place.

The present paper describes a repetition of this reaction, with oxidation of the condensation product; formic and methylvaleric acid and methyl propyl ketone were identified among the oxidation products, showing that the following rearrangement must have taken place either during preparation of the bromide or during the condensation reaction:

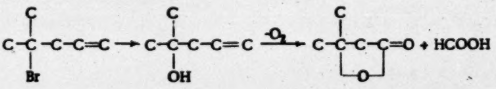


Methyl propyl ketone was evidently obtained by the reaction:

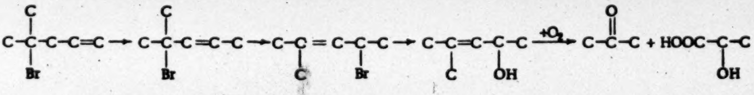


$$C{-}C{-}C{-}\overset{O}{\overset{\|}{C}}{-}C{-}COOH \rightarrow CO_2 + C{-}C{-}C{-}\overset{O}{\overset{\|}{C}}{-}C$$

A study of the oxidation of 4-bromo-4-methylpent-1-ene showed that this tertiary halide only to a small extent undergoes isomerization to β-halide, the formation of which is a result of isomerization of the allyl to the propenyl radical. Among the products of oxidation with 1% aqueous KMnO$_4$ were found β-methyl-β-butyrolactone, formic acid, acetone, and lactic acid, of which the first two products were obtained by hydrolysis and oxidation of the non-isomerized substance



Acetone and lactic acid could only have been formed by oxidation of the γ-rearrangement product:



Acetone could have been obtained by oxidation of the product of elimination of HBr from the bromide, but this could not have taken place under the conditions of the oxidation reaction; it takes place only after several hours of boiling of the bromide with strongly alkaline solutions [10].

The small degree of isomerization of the allyl into the propenyl radical was evidently not augmented by the action of the Grignard reagents on this bromide, and this was the reason why this halide was not, in contrast to 4-bromo-4-propylhepta-1,6-diene, able to enter into the Grignard-Wurtz reaction.

A stronger tendency towards isomerization of allyl to propenyl radicals in presence of Grignard reagents is observed as the number of allyl groups in the bromide molecule increases, as in the cases of 4-bromo-4-methylpent-1-ene and 4-bromo-4-propylhepta-1,6-diene. This corresponds with the enhancement of this type of isomerization observed in the dehydration of allylic alcohols and glycols. We know [11] that the isomerization of allyl to propenyl radicals has never been observed in the dehydration of dimethylallylcarbinol, whereas dehydration of 1,1,6,6-tetraallylhexanediol [12] gives 1,1,6,6-tetrapropenylhexa-1,5-diene.

EXPERIMENTAL

1. Reaction of the Grignard reagent from dimethylallylmethyl bromide with methyl bromide. 120 g of the bromide was added gradually to 16 g of activated magnesium at 10°, and methyl bromide was passed into the product. After the usual treatment, and after elimination of the ether, a small yield of product (3.5 g) was obtained, boiling at 70-80°. After hydrogenation it had b.p. 73-80°, n_D^{20} 1.3761, d_4^{20} 0.6684. Owing to its small amount, and to the presence therein of fluorescent admixtures, the product could not be subjected to spectrum analysis, but it seems probable from its physical constants, given above, that it is isohexane. The ethereal distillate contained isohexene, identified as the dibromide, b.p 98-99°, n_D^{20} 1.5110; d_4^{20} 1.5500.

	Found %:	Br 66.09
$C_6H_{12}Br_2$.	Calculated %:	Br 65.53

A variant of this experiment consisted in adding 70 g of dimethylallylmethyl chloride to a Grignard compound prepared from 24 g of magnesium and methyl chloride. The mixture, after the usual treatment, gave 3 g of a product which after hydrogenation had b.p. 70-80°, d_4^{20} 0.6672, n_D^{20} 1.3765, i.e., it was the same as obtained in the preceding experiment; 28 g (40%) of chloride was recovered unchanged from the reaction mixture. The process was repeated in presence of $HgCl_2$ as activator. An ethereal solution of CH_3MgBr was added to 74 g of dimethylallylmethylchloride and 10 g of $HgCl_2$, and after the usual treatment 13.5 g of the initial chloride was recovered unchanged, and a crystalline precipitate was obtained, which rapidly darkened on exposure to the air, and appeared to be a mercury-organic compound. 4,4-Dimethylpent-1-ene was not obtained.

2. Reaction of CH_3MgBr with 2-chloro-2-methylpentane. 2-Chloro-2-methylpentane, prepared from the corresponding alcohol and HCl, had b.p. 110-112°, n_D^{20} 1.4105. 131 g of 2-chloro-2-methyl-pentane was added to an ethereal solution of CH_3MgBr prepared from 48 g of magnesium, and after the usual treatment, and elimination of unsaturated products, 16 g of a product (15% yield) was obtained. It had b.p. 78-79°, n_D^{20} 1.3820, d_4^{20} 0.6730, bromine no. 0, found MR_D 34.59, calculated for C_7H_{16} MR_D 34.53; spectrum analysis showed the presence of 2,2-dimethylpentane only in this fraction.

This experiment was repeated, taking 105 g of 2-chloro-2-methylpentane and 8 g of $HgCl_2$ The same product was obtained (12% yield) as in the previous reaction, b.p. 79-80°, n_D^{20} 1.3820, d_4^{20} 0.6727, bromine no. 0.

3. Reaction of CH_3MgBr with 4-bromopent-1-ene. Methylallylcarbinol was prepared as described by Stohr [13]: it boiled at 115-117°. (Stohr gives 115-116°). The corresponding bromide, prepared under the same conditions as for dimethylallylmethyl bromide, boiled at 111-112°, n_D^{20} 1.4520, d_4^{20} 1.2417, experimental MR_D 32.8, calculated for C_5H_9Br MR_D 32.6. The magnesium-organic compound was obtained from methyl bromide and 24 g of activated magnesium, and 55 g of 4-bromopent-1-ene was added gradually to it. The mixture was then left overnight, and was heated at the b.p. of ether for 2 hrs. After the usual treatment 45 g of bromide was recovered unchanged; no fraction corresponding to 4-methylpent-1-ene was obtained.

4. Reaction of $CH_2{=}CH{-}CH_2MgBr$ with 4-bromopent-1-ene. 50 g of 4-bromopent-1-ene was added to $CH_2{=}CH{-}CH_2MgBr$, prepared from 60 g of $CH_2{=}CH{-}CH_2Br$ and 11 g of magnesium (a threefold excess), and the mixture was kept at 30° for 80 hrs. After the usual treatment, and after distilling off the ether, the residue was distilled, giving a product, b.p. 110-125°, n_D^{20} 1.4510, d_4^{20} 1.0653. This fraction appears to consist chiefly of the original bromide, but since the hydrocarbon which might arise in this reaction, 4-methylhepta-1,6-diene, boils within the same range, 110.5-110.9°, the product was treated with alcoholic alkali, in order to remove the original bromide. The whole of the residue reacted with the alkali, 4-methylhepta-1,6-diene not being found.

5. Reaction of $CH_3CH_2CH_2CH(CH_3)MgBr$ with allyl bromide. 50 g of allyl bromide was added to the magnesium-organic compound prepared from 60 g of 2-bromopentane and 16 g of magnesium, and the mixture was heated for 80 hrs at 30°. After the usual treatment, 3.7 g of a product was obtained, b.p. 110-113°, n_D^{20} 1.4150, d_4^{20} 0.7296, and 30 g of allyl bromide was recovered (b.p. 69-71°). Since the density of the product obtained by us was higher than that of 4-methylhept-1-ene (the following constants are recorded for this: b.p. 112.6-113°, d_4^{20} 0.7183, n_D^{20} 1.4099 [14]), and since it gave a qualitative reaction for halogen, it was boiled with sodium, after which its physical constants approximated closely to those of 4-methylhept-1-ene (b.p. 112-113°, d_4^{20} 0.7191, n_D^{20} 1.4105, experimental MR_D 39.08, MR_D calculated for C_8H_{16} 38.68, iodine no.221.2, calculated iodine no. for C_8H_{16} 226.4.

6. Oxidation of 4-bromo-4-methylpent-1-ene. 4-Bromo-4-methylpent-1-ene was prepared from PBr_3 and dimethylallylcarbinol in pyridine at 0°, followed by heating for 3-4 hr. After washing with water and redistilling it boiled at 42-47° at 30 mm, 120-125° at 760 mm, n_D^{20} 1.4650, d_4^{20} 1.2001, experimental MR_D 37.97, MR_D calculated for $C_6H_{11}Br$ 37.21.

40 g of the bromide was oxidized with 1% $KMnO_4$ solution at 0° [15], 80 g of $KMnO_4$ being used. The solution was steam-distilled, to remove neutral products. The aqueous distillate was evaporated down to a volume of 50 ml, and this was saturated with potash. The oily layer was separated and distilled, giving the fractions:

Fraction I, b.p. 58-60°
Fraction II, b.p. 60-70°
Residue, density >1.

Fractions I and II, and the residue, were treated with 2,4-dinitrophenylhydrazine. The fractions gave crystalline precipitates, but the residue did not react. The 2,4-dinitrophenylhydrazone given by Fraction I melted at 123-124°, mixed m.p. with the 2,4-dinitrophenylhydrazone of acetone 123.5-124.5°. The 2,4-dinitrophenylhydrazone of Fraction II melts at 120°.

The residue from steam-distillation of the oxidation products was filtered from MnO_2, acidified, and again steam-distilled. The volatile acids included formic acid (1.176 g), b.p. 103-105°, n_D^{20} 1.3720, NaOH equivalent wt. 88.7, calculated for HCOOH 89.0.

A small amount of lactic acid was also found, identified by the iodoform reaction, and by analysis of its silver salt:

Found %: Ag 55.22
$C_3H_5O_3Ag$. Calculated %: Ag 54.82

Oxidation of dimethylallylcarbinol with 4% $KMnO_4$ did not lead to production of acetone. β,β-Dimethylacrylic acid (oxidation of which gives acetone) is obtained from $(CH_3)_2CBrCH_2COOH$ only by boiling with phenol or KOH [10].

Non-volatile acids. The residue after elimination of volatile acids was evaporated down, treated with 25-30 % sulfuric acid, and extracted with a large volume of ether. The residue after evaporation of the ether was fractionally distilled in vacuum, giving the following fractions:

Fraction I, b.p. 70-75° at 10 mm
Fraction II, b.p 75-78° at 10 mm, d_4^{20} 0.9973; n_D^{20} 1.4430
C 58.54%; H 8.10%; equivalent 109

In addition, a crystalline product, m.p. 68-69°, C 59.9%, H 7.95%, was obtained; its m.p. was not depressed when mixed with dimethylacrylic acid.

Fraction I gave a silver salt, Ag 48.96%, calculated for $C_5H_9O_3Ag$ Ag 48.0%.

Fraction II is a mixture of hydroxyvaleric acid with valerolactone. Valerolactone and dimethylacrylic acid are always formed from the corresponding hydroxyvaleric acid when distilled in vacuum.

7. Examination of the product of reaction of 4-bromo-4-propylhepta-1,6-diene with propyl magnesium bromide. Diallylpropylcarbinol was saturated with dry HBr at 80-90°, to give 4-bromo-4-propylhepta-1,6-diene, 45 g of which was taken with 10 g of magnesium and 50 g of propyl bromide, in boiling ethereal solution, as described in our previous paper [9]. The product (6.2 g , 17% yield) is tridecadiene, b.p. 98-104° at 20 mm, n_D^{20} 1.4484, $C_{13}H_{24}$.

6 g of tridecadiene was oxidized with 1% $KMnO_4$ solution, the MnO_2 was filtered off, and the filtrate was made strongly acid and boiled for several hours in order to effect decarboxylation of any β-keto-acids which might have been formed. The solution was then alkalized and steam-distilled, and the distillate was extracted with ether, to remove neutral products. The ether was distilled off, and the residue was fractionated; practically all of it came over at 98-104° (most of it at 99-101°), yield 1.7 g. This was shown to be methylpropyl ketone, identified as the 2,4-dinitrophenylhydrazone, m.p. 142°, (published m p. 144° [16]), not depressing the m.p. of a known specimen.

The residue from steam-distillation was evaporated down and acidified with dilute sulfuric acid. The layer of acidic products forming was separated, and the aqueous layer was extracted with ether. The acidic layer was dissolved in the ethereal extract, which was dried, the ether was distilled off, and the residue was fractionated, giving 0.4 g of a fraction of b.p. 99-103°, and 2.3 g of a fraction boiling at 191-196° (most of it at 193-194°), n_D^{20} 1.4117. The first fraction gave a precipitate of calomel when treated with mercuric chloride, showing that it was formic acid. The second fraction was α-methyl-valeric acid (recorded constants, b.p. 192-193.6°, n_D^{20} 1.4136 [17]), the silver salt of which was analyzed:

Found %: Ag 47.88
$C_6H_{11}O_2Ag$. Calculated %: Ag 48.4

The amide of this acid melted at 77°, published m.p. 78° [17]. No other acids were found. It follows that 4-bromo-4-propylhepta-1,6-diene does not enter into the reaction, as could have been expected; its rearrangement product 6-bromo-4-propylhepta-1,4-diene reacts instead. The rearrangement may have taken place during the synthesis of the bromide, at the temperatures involved, or it may have occurred during the Grignard-Wurtz reaction.

8. Reaction between γ-butenyl magnesium bromide and 5-chloro-5-butylnonane. PBr_3 in pyridine and but-3-en-1-ol were allowed to react under the conditions described by Juvala [18], to give butenyl γ-bromide, b.p. 97-99°, d_4^{20} 1.3247; n_D^{20} 1.4638; published constants [18]: b.p. 98.5-99° at 758 mm; d_4^{20} 1.3230; n_D^{20} 1.46215 [18].

The magnesium-organic compound was prepared from 30 g of butenyl γ-bromide and 5.3 g of magnesium in 60 ml of ether. The ether was distilled off at $<$ 90°, and 36 g of 5-chloro-5-butylnonane was added drop by drop during 5 hr at 70-80°, and the mixture was left overnight. It was then subjected to the usual treatment, and the ether layer was dried with Na_2SO_4. The ether was then distilled off, and the residue was vacuum distilled. The sole product was that of elimination of HBr from the bromide, viz., 5-butylnon-4-ene, b.p. 91-93° at 10 mm, n_D^{20} 1.4398. Under the same conditions butyl bromide and 5-chloro-5-butylnonane give tetrabutylmethane, in 15% yield.

Raman spectrum analyses were performed by M. I. Batuev.

SUMMARY

1. It has been shown that primary, secondary, and tertiary γ-halides (4-bromobut-1-ene, 4-bromopent-1-ene, and 4-bromo-4-methylpent-1-ene) do not enter into the Grignard-Wurtz reaction, as the introduction of a double bond in the γ-position, similarly to its introduction in the α-position to the halogen atom, greatly lowers the reactivity of the halides, as compared with that of the corresponding saturated alkyl halides; introduction of a double bond in the β-position, on the contrary, enhances reactivity.

2. It is shown that the earlier observed reaction of condensation of $n\text{-}C_3H_7MgBr$ with tertiary γ-halide (4-bromo-4-propylhepta-1,6-diene) depended on isomerization of one of the allyl radicals of this halide to a propenyl radical, followed by an allyl rearrangement leading to formation of the corresponding secondary halide (6-bromo-4-propylhepta-1,4-diene).

Received March 28, 1952

Institute of Organic Chemistry
Academy of Sciences USSR

LITERATURE CITED

[1] V. Krestinsky, J. Russ. Phys. Chem. Soc., 52, 63, 75, 85 (1920).

[2] P. K. Kogerman, J. Am. Chem. Soc., 52, 5060 (1930).

[3] M. S. Kirrmann, Comptes, rend., 184, 1178 (1927).

[4] M. S. Karash and F. Fuchs, J. Am. Chem. Soc., 65, 505 (1943).

[5] R. Ya. Levina, J. Gen. Chem., 11, 411 (1941); 11, 523 (1941).

[6] W. G. Young and I. D. Roberts, J. Am. Chem. Soc., 66, 2131 (1944); 67, 319 (1945); 67, 871 (1945); 68, 1472 (1946).

[7] H. Schinz, H. L. Simon, Helv. chim. Acta 28, 774 (1945).

[8] G. Goethals, Bull. Soc. Chim. Belg., 46, 409 (1937).

[9] A. D. Petrov and E. A. Chernyshev, Doklady, 67, No. 6, 1045 (1949).

[10] K. Auwers, W. Mauss, Ber., 61, 2549 (1928).

[11] Bacon, Farmer, J. Chem. Soc., 1065 (1937); Ya. M. Slobod et al, J. Gen. Chem.8, 241 (1938).

[12] M. A. Cheltsova and A. D. Petrov, Doklady, 58, No. 7 (1947).

[13] L. Stohr, Ber., 72, 1138 (1939).

[14] R. D. Obolentsev, Physical constants of the components of light motor fuel oils, p. 126, Gastoptekhizdat, (State Sci.-Tech. Press of Petroleum and Light Fuel Literature), 1943.

[15] A. Shirokov, J. Prak. Chem., 23, 196 (1881).

[16] R. Shrainer and R. Fewson, Systematic qualitative analysis of organic compounds, p. 259. In. lit. 1950.

[17] K. Levene, H. Mikeska, J. Biol. Chem., 84, 571 (1929); K. Levene, R. Marker, Loc. cit. 98, 1 (1932).

[18] A. Juvala, Ber., 63, 1992 (1930).

RESEARCHES ON ACETYLENIC ALCOHOLS AND GLYCOLS

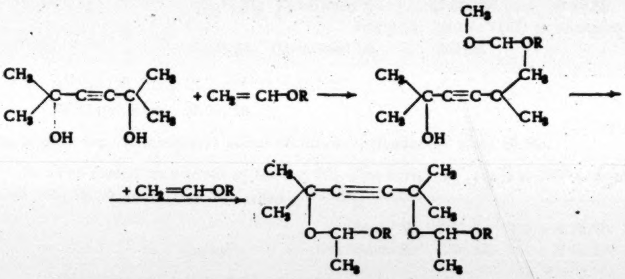
PART 2. SYNTHESIS OF MONO- AND DI-ACETALS OF TETRAMETHYLBUTINDIOL

M. F. Shostakovsky and A. V. Bogdanova

The present paper is a continuation of a study of acetylenic alcohols and glycols, which was initiated with propargyl alcohol, butindiol, and vinyl ethers, and was extended to tetramethylbutindiol.

Tetramethylbutindiol was studied by Zalkind [1], who investigated its hydrogenation with various catalysts, as well as reactions of addition to its triple bond of phenol [2], and of methanol and acetic acid in presence of HgO and BF_3 [3]. Dehydration of the products of addition of phenol and alcohols gives cyclic products of the furan series. Of the reactions of substitution of hydrogen of the hydroxyl groups of tetramethylbutindiol only that with alcohols was studied, leading to formation of tetramethylbutindiol ethers [4,5]. In connection with this, the preparation of new substitution products of tetramethylbutindiol was thought to be of interest.

The synthesis of mono- and di-acetals of tetramethylbutindiol adds considerably to our knowledge of compounds of this type, and by varying the nature of the acetyleneglycol, on the one hand, and of the vinyl ethers on the other, it affords us the opportunity of obtaining different products having a wide range of physical and chemical properties. The reaction of tetramethylbutindiol with vinyl ethers proceeds as follows:



The mono- and di-acetals of tetramethylbutindiol which are formed are of interest for the study of the mechanism of decomposition of substances of this class, due to thermal and other factors. The present paper describes catalytic and thermal methods for the synthesis of acetals of tetramethylbutindiol [6]. The reaction proceeds smoothly, giving good yields of acetals. Certain experimental difficulties were encountered in the process of isolating certain of the monoacetals by repeated vacuum distillation, owing to their instability; thus we could not isolate the monoethyl and monoctyl acetals of tetramethylbutindiol altogether free of saturated products. Our experiments showed that both the catalytic and the thermal methods of synthesis give both mono- and di-acetals depending on the temperature and duration of reaction, and on the amount of catalyst taken. The reaction may be interrupted at the stage of monoacetal production even when excess of vinyl ether is present.

The structure of the acetals was established by a study of their hydrolysis products. In view of the differences in the velocity of hydrolysis of different acetals, the conditions of hydrolysis [6] were varied accordingly (sealed tube, temperature, duration, concentration of acid).

EXPERIMENTAL*

Reagents used. Tetramethylbutindiol was prepared by Shikhiev by Babayan's modification [8] of

---

* Senior Laboratory Technician M. S. Egorova took part in the work.

Favorsky's method [7], from acetone and acetylene. After purification it boiled at 121-123° at 7 mm, and melted at 94.5-95.5°. The vinyl ethers were purified by means of the procedure recommended by the Laboratory of Vinyl Compounds [9]; they had the following constants:

Vinyl butyl ether; b.p. 93.5-94°, n_D^{20} 1.4020.
Vinyl ethyl ether; b.p. 36-36.5°, n_D^{20} 1.3775.
Vinyl octyl ether; b.p. 59-60° at 10 mm, n_D^{20} 1.4275.

Preparation of the mono- and di-butyl acetals of tetramethylbutindiol

$(CH_3)_2-C(OH)-C\equiv C-C(CH_3)_2-OCH(CH_3)-OC_4H_9$ and

$C_4H_9O-(CH_3)-HCO-(CH_3)_2C-C\equiv C-C(CH_3)_2-OCH(CH_3)-OC_4H_9$

1. In an autoclave. 35.5 g (0.25 mole) of crystalline tetramethylbutindiol and 50.0 g of vinyl butyl ether (0.5 mole) were heated in a 1 liter rotating autoclave for 9 hrs at 96-110°, to give 83 g of a clear liquid product, vacuum distillation of which gave:

Fraction I, b.p. up to 76° at 17 mm;	16.0 g
Fraction II, b.p. 76-136° at 14 mm;	22.2 g
Fraction III, b.p. 136-164° at 14 mm;	32.4 g
Residue	7.5 g

Fraction I was vinyl butyl ether, b.p. 93-94°, n_D^{20} 1.4020.

Fraction II deposited 5.6 g of crystalline tetramethylbutindiol, m.p. 92-94°.

The residue of Fraction II and Fraction III gave two products, one of which had b.p. 121-122° at 7 mm, n_D^{20} 1.4440; d_4^{20} 0.9175; found MR_D 69.93; calculated for $C_{14}H_{26}O_3 \models$ MR_D 69.60.

Found %: C 69.73; 69.51; H 10.77, 10.90
$C_{14}H_{26}O_3$. Calculated %: C 69.40; H 10.82
Found M: 249.8; 247.3 (cryoscopically, in benzene)
$C_{14}H_{26}O_3$. Calculated M: 242.35

Hydrolysis and determination of acetal*

% Acetal found: 96.68, 96.23.

The product was the monobutyl acetal of tetramethylbutindiol; yield 58.8%.

The second product (12 g) had the following constants: b.p. 146-147° at 8 mm, n_D^{20} 1.4380; d_4^{20} 0.9150; found MR_D 98.26; calculated for $C_{20}H_{38}O_4 \models$ MR_D 99.06.

Found %: C 70.25; 70.37; H 11.28; 11.19
$C_{20}H_{38}O_4$. Calculated %: C 70.13; H 11.18

Hydrolysis and determination of acetal

% Ether found: 96.25, 96.54.

The product was the dibutyl acetal of tetramethylbutindiol; yield 16.6%.

2. Catalytic method. A solution of 35.5 g (0.25 mole) of tetramethylbutindiol in 50.0 g of dioxan was placed in a flask fitted with a stirrer, a thermometer, a reflux condenser, and a dropping-funnel, and 50 g (0.5 mole) of vinyl butyl ether was added drop by drop during an hour, as well as 3 drops of concentrated sulfuric acid, the temperature being maintained at 53-56°. The mixture was then heated at 65-70° for 3.5 hrs, after which it was dried over potash. It was then filtered, the filtrate was distilled, giving 56.3 g of dioxan with some vinyl butyl ether, and the residue was vacuum distilled:

Fraction I, b.p. 73-132° at 8 mm;	41 g
Fraction II, b.p. 132-154° at 8 mm;	16.3 g
Residue	7.6 g

10 g of vinyl butyl ether was collected in a cooled receiver, and 1 g of crystalline tetramethylbutindiol was

---

* Hydrolysis was effected by heating a weighed sample in a sealed tube with 25 ml of 0.5 N H_2SO_4.

separated from Fraction I.

The mono- and di-butyl acetals of tetramethylbutindiol were isolated from the liquid residues of Fractions I and II. The monobutyl acetal had b.p. 122-123° at 7 mm, n_D^{20} 1.4438; d_4^{20} 0.9170; yield 50 g. (84.9%) and the dibutyl acetal had b.p. 147-148° at 7 mm, n_D^{20} 1.4380; d_4^{20} 0.9156; yield 2.4%.

3. The dibutyl acetal of tetramethylbutindiol was prepared as described in 2 above, taking the same amounts of reagents, and under the same conditions, with the difference that the duration of reaction was increased to 8 hrs. The product, yield 66%, boiled at 143-144° at 4 mm, n_D^{20} 1.4375; d_4^{20} 0.9146.

Synthesis of the mono- and di-octyl acetals of tetramethylbutindiol

$(CH_3)_2{-}C(OH){-}C{\equiv}C{-}C(CH_3)_2{-}OCH(CH_3){-}O(CH_2)_7CH_3$ and

$CH_3(CH_2)_7O{-}(CH_3)CHO{-}(CH_3)_2C{-}C{\equiv}C{-}C(CH_3)_2{-}OCH(CH_3){-}O(CH_2)_7CH_3$

42 g of vinyl octyl ether was added drop by drop to a solution of 18.5 g of tetramethylbutindiol in 25 g of dioxan containing 4 drops of hydrochloric acid, and the mixture was heated at 75-80° for 6 hrs. The product was treated with potash, and vacuum distilled, giving:

Fraction I, b.p. 25-124° at 36 mm;	28.7 g.
Fraction II, b.p.124-153° at 11 mm;	3.5 g.
Fraction III, b.p. 153-183° at 11-3 mm;	32.8 g.
Fraction IV, b.p. 183-187° at 3 mm;	18.0 g.
Residue	3.4 g.

Fraction I was dioxan, b.p. 101-101.5°, m.p. 10°. Fraction II deposited 1.0 g of tetramethylbutindiol, m.p. 93-94° (from ethanol Fraction III gave, after repeated redistillation, 21.5 g of a liquid product, having the following constants: b.p. 138-138.2° at 3 mm, n_D^{20} 1.4420; d_4^{20} 0.8713; found MR_D 90.64; calculated for $C_{18}H_{34}O_3\,|\!\!\equiv$. MR_D 88.07.

Found M: 282.2; 287.4 (cryoscopic, in benzene)

$C_{18}H_{34}O_3$. Calculated M: 298.45

Hydrolysis and determination of acetal

% Acetal found: 92.38

The Fraction contains 92.38% of the monooctyl acetal of tetramethylbutindiol, which was thus obtained in 62.0% yield.

16 g of a product having the following constants was isolated from Fraction IV: b.p. 184-186° at 1 mm, n_D^{20} 1.4460; d_4^{20} 0.8905; found MR_D 136.2; calculated for $C_{28}H_{54}O_4\,|\!\!\equiv$ MR_D 136.01.

Found %: C 74.02; 73.80; H 11.62; 11.90

$C_{28}H_{54}O_3$. Calculated %: C 73.96; H 11.97

Found M: 450.0; 436.2 (cryoscopic, in benzene)

$C_{28}H_{54}O_4$. Calculated M: 454.71

Hydrolysis and determination of acetal

% Acetal found: 94.91, 95.14.

This product is the dioctyl acetal of tetramethylbutindiol, yield 30.3%.

Synthesis of the diethyl acetal of tetramethylbutindiol

$C_2H_5O{-}(CH_3)HCO(CH_3)_2\,C{-}C{\equiv}C{-}C(CH_3)_2{-}OCH(CH_3){-}OC_2H_5$

36.0 g (0.5 mole) of vinyl ethyl ether was added, under similar conditions to those described above, to a solution of 35.5 g (0.25 mole) of tetramethylbutindiol in 50 g of dioxan at 43-45°, in presence of 4 drops of hydrochloric acid. After heating at 65-70° for 5 hrs the dioxan was distilled off, and the residue was vacuum-distilled:

Fraction I, b.p. 110-120° at 9 mm;	11.5 g
Fraction II, b.p. 120-132° at 9 mm;	44.5 g
Residue	10.0 g

Fractions I and II were redistilled, giving 40 g of a product having the following constants: b.p. 103.5-105° at 2 mm, n_D^{20} 1.4320; d_4^{20} 0.9125; found MR_D 81.41; calculated for $C_{16}H_{30}O_4 \vert\!\equiv$ MR_D 80.6.

	Found %:	C 67.44; 67.54,	H 10.49; 10.36
$C_{16}H_{30}O_4$.	Calculated %:	C 67.11;	H 10.56
	Found M:	280.8; 256.0 (cryoscopic, in benzene)	
$C_{16}H_{30}O_4$.	Calculated M:	286.4.	

Hydrolysis and determination of acetal

% Acetal found: 93.28, 94.37

The product was the diethyl acetal of tetramethylbutindiol; yield 56.0%.

SUMMARY

1. A study has been made of the reactions of tetramethylbutindiol with vinyl ethyl, butyl, and octyl ether, leading to production of mono- and di-acetals of tetramethylbutindiol, in yields of up to 85%.

2. Five new acetals were thus prepared, and their structure was established by a study of their hydrolysis products.

3. The diacetals are formed through the intermediate stage of mono-acetals, the yield of which depends on the amount of vinyl ethers taken for the reaction, and on its duration.

Received November 20, 1951

Institute of Organic Chemistry
Academy of Sciences USSR

LITERATURE CITED

[1] Yu. S. Zalkind and A. V. Paschikov. J. Russ. Phys. Chem. Soc., 45, 1875 (1913), 46, 1527 (1914); 48,1830 (1916); J. Gen. Chem., 3, 91 (1933).

[2] Yu. S. Zalkind and O. F. Moiseeva; J. Gen. Chem., 20, 888 (1950).*

[3] J. F. Froming and G. F. Hennion, J. Am. Chem. Soc., 62, 563 (1940).

[4] G. Dupont, Comptes. rend., 152, 197 (1911).

[5] Yu. S. Zalkind and L. P. Chogogidze-Chanturishvili, J. Gen. Chem., 20, 719 (1950).**

[6] M. F. Shostakovsky and N. A. Gershtein, J. Gen. Chem., 16, 937 (1946); 18, 451 (1948); 18, 1996 (1948).

[7] A. E. Favorsky and M. Skosarevsky, J. Russ. Phys. Chem. Soc., 37, 643 (1900).

[8] A. Babayan, B. Akopyan, and R. Guli-Kevkyan, J. Gen. Chem., 9, 163 (1939); 10, 1177 (1940).

[9] M. F. Shostakovsky and E. N. Prilezhaeva, J. Gen. Chem., 17, 1130 (1947).

---

* See Consultants Bureau English Translation, p. 923.

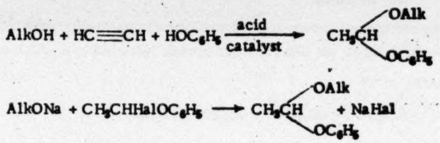
** See Consultants Bureau English Translation, p. 757.

INDIRECT VINYLATION OF ALIPHATIC ALCOHOLS

M. F. Shostakovsky, B. I. Mikhantyev, and N. N. Ovchinnikova

Direct vinylation with acetylene of primary and secondary C_1–C_5 alcohols proceeds smoothly at 140-160° in presence of KOH, giving yields of up to 95% of the corresponding ethers [1]. Tertiary alcohols and alcohols with double or triple bonds do not react with acetylene under the same conditions. The vinylation of tertiary, and more particularly of unsaturated, aliphatic alcohols is of considerable theoretical and practical interest.

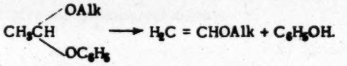
The proposed indirect method for vinylation of tertiary and ethylenic aliphatic alcohols follows directly from the researches of Shostakovsky [2] and his co-workers in the Laboratory of Vinyl Compounds, who found that alcohols or alkoxides or alkaline solutions of alcohols react with vinyl phenyl or α-halogenoethyl phenyl ethers to give mixed alkyl phenyl acetals, as follows:



$$AlkOH + HC{\equiv}CH + HOC_6H_5 \xrightarrow[\text{catalyst}]{\text{acid}} CH_3CH(OAlk)(OC_6H_5)$$

$$AlkONa + CH_3CHHalOC_6H_5 \longrightarrow CH_3CH(OAlk)(OC_6H_5) + NaHal$$

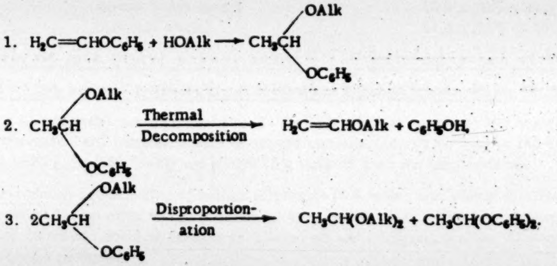
The formation of vinyl alkyl ethers by the thermal decomposition of alkyl phenyl acetals was shown to take place [2], as follows:



$$CH_3CH(OAlk)(OC_6H_5) \longrightarrow H_2C = CHOAlk + C_6H_5OH.$$

The reaction was also confirmed by the work of other authors [3], who ascribed the decomposition of the acetals to the catalytic action of inorganic acids or their salts, and of sulfanilic acid or anilsulfate. The yields of vinyl ethers so obtained varied from 50-74%.

The reagents used in our research were vinyl phenyl ether and secondary and tertiary butyl and allyl alcohols, from which we synthesized the corresponding mixed acetals, heating of which on an air-bath in all cases led to decomposition of the acetals, with formation of the vinyl ether of the given alcohol, together with phenol. Vacuum distillation of the mixed alcohols at pressures of 25-35 mm gave rise to alkyl vinyl ethers, dialkyl acetals, diphenyl acetal, and phenol. Distillation at 3-5 mm pressure gave only disproportionation products. The transformations observed may be represented by the following reactions:



$$1.\ H_2C{=}CHOC_6H_5 + HOAlk \longrightarrow CH_3CH(OAlk)(OC_6H_5)$$

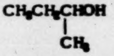
$$2.\ CH_3CH(OAlk)(OC_6H_5) \xrightarrow[\text{Decomposition}]{\text{Thermal}} H_2C{=}CHOAlk + C_6H_5OH,$$

$$3.\ 2CH_3CH(OAlk)(OC_6H_5) \xrightarrow[\text{ation}]{\text{Disproportion-}} CH_3CH(OAlk)_2 + CH_3CH(OC_6H_5)_2.$$

where Alk is secondary or tertiary butyl or allyl.

It appears from the above reation schemes that aryl alkyl acetals are the starting point for the preparation not only of the corresponding symmetrical acetals [4-5] but also of vinyl ethers of secondary and tertiary alcohols and unsaturated alcohols.

TABLE 1 Specification of initial reagents

Compound	b.p. °C/ 760 mm	n_D^{20}	d_4^{20}	Remarks
sec.-Butanol  $CH_3CH_2\underset{\substack{\vert \\ CH_3}}{C}HOH$	97-98	1.3952	0.8075	
tert.-Butanol $(CH_3)_3COH$	82.5	–	–	m.p. 25.3° n_D^{20} 1.3824 d_4^{20} 0.7775
Allyl alcohol $CH_2{=}CHCH_2OH$	96-97	1.4132	0.8550	
Vinyl phenyl ether $CH_2 = CHOC_6H_5$	155-156	1.5224	0.9768	
α-Chloroethyl phenyl ether $CH_3CHClOC_6H_5$		1.5225	1.1150	b.p. 93-94/22 mm

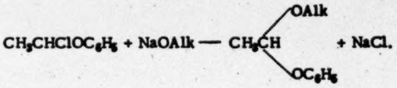
Acetal formation took place at temperatures 2-3°, lower than the boiling point of the corresponding vinyl alkyl ether, as this gave the highest yields of mixed acetals (25-32%). Vinyl alkyl ethers are obtained in yields of up to 77%. The reaction of indirect vinylation amounts to transetherification of aryl radicals of vinyl aryl ethers by alkyl radicals, as follows:

$$H_2C{=}CHOC_6H_5 + HOAlk \longrightarrow$$

$$\longrightarrow H_2C{=}CHOAlk + C_6H_5OH,$$

which is of special importance in the case of unsaturated alcohols, direct vinylation of which has not yet been achieved.

In order to raise the yield of aryl alkyl acetals we prepared them from readily available α-chloroethyl phenyl ether [6] and the appropriate alkoxides, by the reaction:



$$CH_3CHClOC_6H_5 + NaOAlk \text{ — } CH_3CH\begin{cases}OAlk\\ OC_6H_5\end{cases} + NaCl.$$

Vacuum distillation of the reaction mixture gave up to 40% yields of aryl alkyl acetals, which were further treated as above, i.e., the mixed acetals were decomposed to give vinyl alkyl ether and phenol, or disproportionated to give the symmetrical acetals.

EXPERIMENTAL

The aryl alkyl acetals were prepared in a flask fitted with a stirrer, a thermometer, and a reflux condenser, the temperature being regulated by a water-bath. An example of a synthesis is given below. The physical constants of the reagents used are given in Table 1.

tert.-Butyl phenyl acetal. 0.2 g of P_2O_5 catalyst (or concentrated H_2SO_4 or HCl) was added to a mixture of 37 g of tert.-butanol (0.5 mole) and 60 g of vinyl phenyl ether (0.5 mole) at 30°. The temperature rose to 75-80° after 30 minutes, and the mixture turned faint yellow. After it had cooled to room temperature the mixture was treated with potash and with sodium, and then vacuum-distilled. Redistillation of the fractions obtained gave the following individual products:

tert.-Butyl phenyl acetal	26.2 g (27% yield)
Di-tert.-butyl acetal	12.2 g (28% yield)
Diphenyl acetal	13.4 g (25% yield)

Hydrolysis of tert.-butyl phenyl acetal, and determination of its percentage content*

30.9 ml of 0.1 N-I_2 was used to titrate 25 ml of bisulfate % Acetal found: 95.55, 96.11

25 g of tert.-butyl phenyl acetal (see Table 2 for physical constants) was heated in a Favorsky flask fitted with a thermometer, and connected with an upright condenser, on an air-bath at 140-150°, giving vinyl tert.-butyl ether (9.63 g., or 75% yield) and phenol (6 g isolated from the tarry residue).

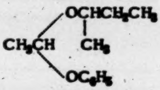
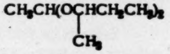
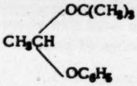
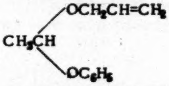
Allyl phenyl acetal. 40 g of sodium allyloxide (0.5 mole was placed in a flask, and 78.3 g (0.5 mole of α-chloroethyl phenyl ether was added drop by drop during 1 hour. The temperature of the mixture rose to 62°, and its color darkened. Solid products were filtered off and discarded, and the filtrate was distilled at 3 mm, giving the following products:

---

* Hydrolysis was effected by heating weighed samples of the acetals in a sealed tube with 25 ml of 0.5N-H_2SO_4.

TABLE 2

Characteristics of the acetals obtained

Compound	Yield % ***	B.p. °C	Pressure mm	d_4^{20}	n_D^{20}	MR_D found, calc.	M found calc.	% C found calc.	% H found calc.
sec.-Butyl phenyl acetal* 	32-40	57-60	5	0.9552	1.4786	57.308 57.481	193.02 194.264	74.02 74.19	9.36 9.34
Di-sec.-butyl acetal*  $CH_3CH(O\underset{CH_3}{CH}CH_2CH_3)_2$	27-35	73-74	25	0.8231	1.4048	51.548 51.886	173.18 174.276	68.94 68.91	12.68 12.72
tert.-Butyl phenyl acetal* 	27-36	53-55	5	0.9560	1.4790	57.839 57.481	195.00 194.264	74.28 74.19	9.17 9.34
Di-tert.-butyl acetal $CH_3CH[OC(CH_3)_3]_2$	28-31	63-64	13	0.8246	1.4054	51.085 51.886	174.30 174.276	68.74 68.91	12.85 12.72
Allyl phenyl acetal* 	25-30	65-67	8	0.9613	1.4908	51.547 52.356	178.35 178.222	74.14 74.13	7.82 7.92
Diallyl acetal $CH_3CH(OCH_2CH{=}CH_2)_2$	22-26	147-149	760	0.8482	1.4208	42.138 41.636	141.98 142.192	67.58 67.57	9.76 9.92
Diphenyl acetal** $CH_3CH(OC_6H_5)_2$	25-23	144-146	35	1.0805	1.5542	64.009 63.076	216.03 214.252	78.44 78.48	6.87 6.59

---

* Not previously prepared.

** Diphenyl acetal was obtained by the disproportionation of all three aryl alkyl acetals. In Table 2 we give data relating to diphenyl acetal obtained from allyl phenyl acetal.

*** In the column "Yield %" the first figure refers to the yield of products obtained by the reaction of vinyl phenyl ethers with alcohols, and the second to acetals obtained from alkoxides and chloro-ether.

Allyl phenyl acetal	27 g (30% yield)
Diallyl acetal	9.2 g (26% yield)
Diphenyl acetal	12.3 g (23% yield)

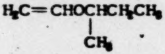
Hydrolysis of allyl phenyl acetal, and determination of its percentage content

31.2 ml of 0.1 N-I_2 was used to titrate 25 ml of bisulfite % Acetal found: 95.97, 98.27.

Decomposition of 27 g of allyl phenyl acetal gave 9.81 g of vinyl allyl ether (77% yield). Analytical data and physical constants of the compounds obtained are given in Tables 2 and 3; the physical constants agree

TABLE 3

Characteristics of the vinyl alkyl ethers obtained

Compound	Yield (%)	B.p. °C/760 mm	d_4^{20}	n_D^{20}	MR_D found, calc.	M found, calc.	%C found, calc.	%H found calc.
Vinyl sec.-butyl ether  $H_2C{=}CHOCH(CH_3)CH_2CH_3$	75.8	81-81.5	0.7720	1.3970	31.397	100.65	72.01	12.03
					31.204	100.156	71.95	12.08
Vinyl tert-butyl ether $H_2C{=}CHOC(CH_3)_3$	75.0	75-75.3	0.7726	1.3978	31.308	100.27	71.85	12.41
					31.204	100.156	71.95	12.08
Vinyl allyl ether $H_2C{=}CHOCH_2CH{=}CH_2$	77.0	66-66.7	0.7900	1.4062	26.219	84.29	71.53	9.44
					26.079	84.124	71.39	9.59

closely with those quoted in the literature [7]. The structure of the three new aryl alkyl acetals was also established by hydrolysis.

A comparison of the two methods of preparation of aryl alkyl acetals, from alcohols and vinyl phenyl ethers, and from alkoxides and -chloroethyl phenyl ether, shows that the latter method gives somewhat higher yields (36%, as compared with 27% of tert.-butyl phenyl acetal by the former method).

SUMMARY

1. A method has been worked out for the indirect vinylation of tertiary and unsaturated aliphatic alcohols.

2. sec.-Butyl phenyl acetal, tert.-butyl phenyl acetal, and allyl phenyl acetal have been synthesized; they have not previously been described.

LITERATURE CITED

[1] A. E. Favorsky and M. F. Shostakovsky, J. Gen. Chem., 13, 1-2, 1 (1943).

[2] M. F. Shostakovsky, J. Gen. Chem., 20, 4, 608 (1950).*

[3] A. E. Arbuzov, J. Russ. Phys. Chem. Soc., 40, 631 (1908); 41, 294 (1909); 54, 462 (1923); A. E. Chichibabin, J. Russ. Phys. Chem. Soc., 41, 295 (1909); I. I. Ostromyslensky, J. Russ. Phys. Chem. Soc., 47, 1494 (1915).

[4] M. F. Shostakovsky and N. A. Gershtein, J. Gen. Chem., 16, 6, 937 (1945); 18, 3, 451 (1948).

[5] J. W. Copenhaver, M. H. Bigelow, Acetylene and carbon monoxide chemistry, N. Y., U.S.A. (1949).

[6] M. F. Shostakovsky and A. V. Bogdanova, J. Gen. Chem., 20, 7, 1325 (1950).

[7] H. D. Hinton, J. A. Nieuland, J. Am. Chem. Soc., 52, 2892 (1930).

Received December 25, 1951

Institute of Organic Chemistry
Academy of Sciencies, USSR

---

* See Consultants Bureau English Translation, p. 643.

** See Consultants Bureau English Translation, p. 1379.

METALLO-ORGANIC "BIURET" COMPLEXES OF PROTEIN BREAKDOWN PRODUCTS

K. T. Poroshin

The study of the processes and products of breakdown of proteins is attracting ever increasing attention. Among the publications of numerous authors who have worked on this subject, the most important are those of Zelinsky and Sadikov [1], Perov [2], Reznichenko [3], and Blagoveshchensky [4]. Work on the problems of breakdown of natural and synthetic high-molecular compounds other than proteins has been done by Korshak and coworkers [5] (polyamides and polyesters), Ivanov, Kaverzneva, and Golova [6] (cellulose), and Knunyants and Rogovin[7] (polycaprolactam).

Among the many methods applicable to the study of processes and products of protein degradation, that depending on the investigation of metallo-organic "biuret" complexes may be of considerable value. The researches of Gavrilov et al., and our own work [8], have opened up promising prospects for the further study of the structure of protein macromolecules. The present paper describes the results of a spectrophotometric study of solutions of copper "biuret" complexes of protein degradation products. The products studied were peptones ("Witte", "Farmakon", and "Siegfried"), and hydrolyzate-peptones from legumin and glycinin, as well as for two protein derivatives of the "proto-acid" type.

Hydrolyzate-peptones from proto-acids, legumin, and glycinin were prepared by hydrolysis with 0.1% hydrochloric acid, by the method described by the authors [9]. The proteins (proto-acids) taken have already been the subjects of detailed chemical and physico-chemical studies [10]. The copper "biuret" complexes were prepared as follows. 3% Caustic soda was added to 100 mg of peptone or hydrolyzate-peptone in amount sufficient to dissolve it, and the volume was made up to 100 ml. 0.25 M Copper acetate was then added until a permanent precipitate of hydroxide separated. The solution was centrifuged after 1-2 hours, and the intensity of coloration of the supernatent fluid was measured by means of a Koenig-Martens spectrophotometer. The results obtained for copper "biuret" complexes of peptones are given in Table 1.

TABLE 1

Values of absorption of light ε for solutions of copper "biuret" complexes of peptones

Wave-length mμ	"Siegfried" peptone	"Farmakon" peptone	"Witte's" peptone
480	0.1275	0.1509	0.1567
505	0.2107	0.2109	0.2404
530	0.2612	0.2492	0.2712
540	0.2595	0.2550	0.2793
550	0.2580	0.2603	0.2775
560	0.2469	0.2534	0.2705
580	0.2337	0.2314	0.2527
610	0.1339	0.1915	0.2135
630	0.1597	0.1634	0.1877
690	0.0987	0.0887	0.0987
730	0.0414	0.0503	0.0594

The spectrophotometric absorption curves are given in Fig. 1; it may be concluded from an analysis of the data of Table 1 and Fig. 1 that the various peptones have different absorption maxima, and that the absorption curves are of different types. The absorption maxima are at 530 mμ for Siegfried peptone, at 540 mμ for Witte's peptone, and at 550 mμ for "Farmakon peptone. The magnitude of absorption for Witte's peptone differs from that for the other two. The spectrophotometric results thus reveal differences in the structures of the three peptones.

The results obtained similarly are shown in Table 2 and Fig. 2, from which it appears that the curves obtained for proto-acid peptones are of the same type, with absorption maxima at 550 mμ. Only small differences in intensity of absorption are found, the greatest difference, at 505-530 mμ, not exceeding 0.0111.

A somewhat different picture is observed with the hydrolyzate-peptones from legumin and glycinin. Solutions of the "biuret" complex from legumin or glycinin have absorption maxima at 540 and 550 mμ, respectively, and the shape of the curves differs. At certain wavelengths a difference in the intensity of absorption is observed, as compared with proto-acid preparations. It is evident that the hydrolyzate-peptones from proto-acid proteins are more homogeneous than are those from legumin and glycinin.

Our experiments show that various forms of primary degradation of proteins, such an enzymatic (pepsin)

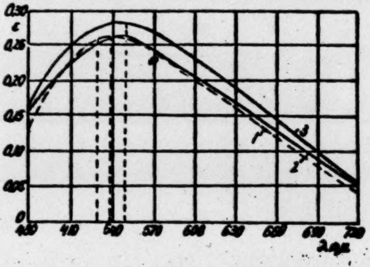


Fig. 1. Spectrophotometric curves for copper "biuret" complexes: 1 - Siegfried peptone; 2 - Farmakon peptone; 3 - Witte's peptone.

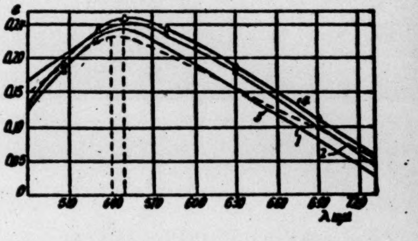


Fig. 2. Spectrophotometric absorption curves for copper "biuret" complexes: 1 - hydrolyzate-peptone from glycinin; 2 - hydrolyzate-peptone from caseinic acid; 3 - hydrolyzate-peptone from legumin; 4 - hydrolyzate-peptone from pea-seed protein.

TABLE 2

Values of ε for solutions of copper "biuret" complexes from protein hydrolyzate-peptones prepared from proteins.

Wave-length mμ	Caseinic acid hydrolyzate	Pea protein hydrolyzate (proto-acid)	Legumin hydrolyzate	Glycinin hydrolyzate
480	0.1283	0.1378	0.1517	0.1648
505	0.1797	0.1908	0.1830	0.2004
530	0.2285	0.2396	0.2205	0.2302
540	0.2417	0.2497	0.2300	0.2372
550	0.2503	0.2572	0.2282	0.2408
560	0.2473	0.2538	0.2204	0.2330
580	0.2331	0.2409	0.2033	0.2129
610	0.2048	0.2112	0.1725	0.1738
630	0.1787	0.1870	0.1527	0.1507
690	0.0994	0.1102	0.0978	0.0905
730	0.0457	0.0608	0.0560	0.0312

TABLE 3

Amount of copper, in mg., needed for the formation of the red complex of caseinic acid and its hydrolyzates.

Product	Mg of Cu per g of product
1. Caseinic acid	9.2
2. Hydrolyzate obtained by action of pepsin on caseinic acid	18.8
3. Hydrolyzate obtained by caseinic acid with 0.1% HCl	39.2
4. Hydrolyzate obtained by hydrolysis of caseinic acid with 2% H_2SO_4	56.7

or acid (0.1% HCl, 2% H_2SO_4) hydrolysis, lead to production of compounds giving red copper complexes with an absorption maximum at 550 mμ, as compounds are formed with a longer polyamide (polypeptide) chain than the tripeptide ones existing before hydrolysis. In connection with this we observe a shift of the absorption maximum in the direction of shorter wave-lengths. Thus, for example, if the solution of copper "biuret" complex of caseinic acid exhibited an absorption maximum of 560 mμ before hydrolysis, this maximum was shifted to 550 mμ after degradation of the protein. The amount of peptides in the primary degradation products may be determined by means of the method of differentiated spectrophotometry developed by us [8]. It may be expressed quantitatively as milligrams of copper bound in the red "biuret" complex, and the figures of Table 3 express the variations found in this value in different forms of degradation of the protein.

As has been shown earlier [10], the protein macromolecule consists basically of tripeptides, which make up 92% of the molecule. The amount of peptides giving a red "biuret" complex with copper increases during the early stages of protein degradation. This effect cannot be explained on the basis of a protein macromolecule structure involving only peptides.

SUMMARY

1. The absorption curves of solutions of copper "biuret" complexes of primary degradation products of a number of proteins have been constructed.

2. It is shown that the copper "biuret" complexes derived from proteins of the "proto-acid" type have identical absorption maxima, and equal intensity of absorption.

3. Red copper "biuret" complexes are given by the polypeptides (polyamides) formed during the initial period of primary protein degradation.

Received June 19, 1952

Institute of Organic Chemistry
Academy of Sciences USSR

LITERATURE CITED

[1] N. D. Zelinsky and V. S. Sadikov, Biochem. Z., 136, 211 (1923); 137, 297 (1923); 137, 401 (1923); 138, 156 (1923).

[2] S. S. Perov, Publications of the Protein Laboratory, VASKhNIL,* Nos. 1-8 (1940-1941); ibid, Nos. 1-2 (1940-1941), Acad. Sci. USSR Publ.

[3] M. S. Reznichenko and M. E. Sitnikova, Biokhimia 3, 102 (1938).

[4] A. V. Blagoveshchensky, "Enzymes", Acad. Sci. USSR Publ., 1940.

[5] V. V. Korshak and V. V. Golubev, Bull. Acad. Sci. USSR, Div. Chem. Sci., 379 (1940).

[6] V. V. Korshak and V. A. Zamyatina, Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 6, 609 (1945); V. V. Korshak, Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 1, 51 (1950); V. I. Ivanov and O. P. Golova, ibid, No. 4, 385 (1945); V. I. Ivanov and E. D. Kaverzneva, ibid., No. 5, 492 (1945).

[7] I. L. Knunyants, Z. A. Rogovin, Yu. Romashevskaya, E. Khait, J. Gen. Chem., 17, 9, 987 (1947).

[8] N. I. Gavrilov, A. A. Proadashvili, and A. I. Govorov, Biokhimia, 4, 35 (1939); N. I. Gavrilov, M. I. Plekhan, and N. A. Poddubnaya, Bull. Acad. Sci. USSR, Div. Chem. Sci., 127 (1941); M. I. Plekhan and N. I. Gavrilov, J. Gen. Chem., 18, 1843 (1948); M. I. Plekhan, J. Gen. Chem., 21, 312, 316, 574, 579 (1951); ** K. T. Poroshin, "Researches on High-Molecular Compounds", p. 193 (1949); "Chemistry and Physical Chemistry of High-Molecular Compounds", p. 116 (1952).

[9] K. T. Poroshin, Publications of the Protein Laboratory, Nos. 1-2, Acad. Sci. USSR Publ., 1940-1941.

[10] K. T. Poroshin, Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 5, 972 (1952). ***

---

* All-Union Scientific Research Institute of the Electrification and Mechanization of Agriculture.

** See Consultants Bureau English Translation, pp. 341, 347, 635, and 641.

*** See Consultants Bureau English Translation, p. 855.

BLANK
PAGE

HIGH-MOLECULAR COMPOUNDS

PART 52. REACTIONS OF POLYESTER MACROMOLECULES WITH EACH OTHER

V. V. Korshak and S. V. Vinogradova

The presence of exchange reactions in the process of polycondensation is one of the most characteristic features of reactions of this type [1]. The laws governing the reactions of ester bonds were studied by us, for the case of reaction of low-molecular esters with acids, alcohols, and other esters [2,3,4,5]. The presence of exchange reactions between polyesters and low-molecular alcohols, leading to degradation of the polyester, was demonstrated by us for the reaction between polyhexamethylene sebacate and cetyl alcohol [6]. The reaction of alcoholysis of polyesters has been demonstrated earlier by Flory [7], who did not, however, include this among the series of degradative reactions. Reactions of polyesters with dicarboxylic acid and glycols, involving their degradation, were first shown by one of us together with Golubev [8]. Similar degradative reactions of polyamides with dicarboxylic acids or diamines have been reported much earlier by one of us together with Rafikov [9] and Zamyatina [10].

All these examples, however, related to the reaction of polyesters or polyamides with low-molecular compounds, such as mono- or di-carboxylic acids, or glycols, alcohols, diamines, and other such compounds, which entet, as was shown by us in the study of the kinetics of the reactions of hexamethyleneglycol with sebacic acid [11], only into the initial stages of the polycondensation process, i.e., at the stage at which the polycondensation products are still of low molecular weight. As the process continues these low molecular weight initial products are used up, and the role played by such compounds diminishes correspondingly. It might hence be supposed that the role of degradative reactions should diminish in the terminal stages of polycondensation reactions, but this supposition is contradicted by the finding that the differential curve of distribution of polyamides according to their molecular weights exhibits a sharp maximum, as was shown by one of us with Zamyatina [12]. The presence of a maximum was found by one of us together with Rafikov and Chelnokova for the differential distribution of polyesters according to their molecular weights [13]. These results are in disagreement with Flory's theory [14], and are ascribable to the existence of degradative exchange reactions at all stages of the polycondensation process [12,13]. It follows that the activity of the macromolecules formed at all stages of the polycondensation process is fairly high, in spite of their comparatively high molecular weight.

The high reactivity of macromolecules in the reaction of chain growth was established by us on the basis of a study of the reaction of polycondensation of hexamethyleneglycol with sebacic acid [11]. We found that the growth of the chains in the terminal stages of the polycondensation reaction is due exclusively to reactions between polyester macromolecules. We thought it would be of considerable interest to elucidate the role and significance of exchange, chiefly degradative, reactions in the terminal stages of polycondensation reactions, at which the original substrates are practically absent, so that the reactions can only be between condensation products. With this object we subjected the reaction between two polyesters of different molecular weight, derived from hexamethyleneglycol and sebacic acid.

EXPERIMENTAL

Initial reagents. The initial polyesters were derived from sebacic acid and hexamethyleneglycol. The reaction was conducted by heating the substrates in a stream of nitrogen from which oxygen had been eliminated by passing over a heated copper spiral. The reaction mixture was heated for 4 hrs at 180° and then for 4 hrs at 190-195°, followed by 3 hrs at 225°. It was then heated in vacuum (2 mm) for 30 hrs, during which the temperature was gradually raised to 250°. Two polyesters were obtained: polyester No. 1, from equivalent amounts of acid and glycol, with a molecular weight of 6608, as derived from viscosity measurements of its benzene solution, and polyester No. 2, obtained with a 30% excess of hexamethyleneglycol, molecular weight 1533 (from viscosity of 0.5% benzene solution).

Experimental results. We first performed preliminary experiments on the effect of temperature on the polyesters, in order to be able to select temperatures at which the reaction velocity was high enough for our purposes, but at which thermal degradation of the polyesters did not take place. For this purpose we examined the effect of heating different polyesters at various temperatures for 10 hrs.

Weighed portions of polyesters were placed in tubes, from which the air was then swept with nitrogen, and the tube was evacuated and sealed, and placed in a thermostat, where it was left for 10 hrs at the appropriate temperature. The results are given in Table 1. The initial molecular weight of the polyester, as determined from viscosity of benzene solutions, was 9540. The data given in Table 1 show that considerable degradation takes place during heating, to an extent proportional to the temperature.

TABLE 1

Thermal degradation of polyesters

Temperature °C	100	150	180	200	250
Molecular weight, from viscosity measurements	9540	8170	7500	6820	6130

The curve of Fig.1 shows the connection between temperature and extent of degradation.

The depth of thermal degradation also depended on the molecular weight of the initial polyester. Thus the molecular weight of a polyester fell from 9540 to 6130, i.e., by 36% after 10 hr of heating at 250°, whereas that of a second polyester fell from 6810 to 5500, under the same conditions, a difference of only 19%, and a third from 3270 to 2840, or only 13%. A polyester of molecular weight 6600 was practically unchanged after 35 hrs at 150°, and this temperature was therefore taken as the optimum one for our experiments.

We next determined the time needed for attainment of equilibrium at this temperature. A tube was filled with a mixture of equal weights of polyesters of molecular weights 6608 and 1533, and the viscosity of benzene solutions of the product after various times 150° was determined, as well as the content of terminal groups (OH and COOH); the molecular weights of the products were hence determined. Terminal groups were determined by the method described in an earlier paper [15]. The results are given in Table 2.

It appears from the data of Table 2 that equilibrium is practically achieved after 14 hrs of heating, after which very little further change in molecular weight takes place even after a further 20 hrs. Having thus established the possibility of achieving an equilibrium state of the exchange reaction between the two polyesters, we studied this reaction as a process of degradation of the higher molecular weight polyester No. 1 (M 6608) by the lower molecular weight ester No. 2 (M 1533). The ratio of the initial polyesters taken was such that 0.5 to 100% of polyester No. 2 was taken per part by weight of polyester No. 1. The properties of a range of such mixtures were determined before heating, and are recorded in Table 3.

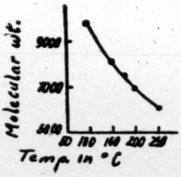


Fig. 1. Thermal degradation of polyester.

TABLE 2

Kinetics of reaction of two polyesters

Serial No.	Duration of heating, hr.	Viscosity of 0.5% solution in benzene	Molecular weight, from viscosity	Ml of 0.02 N NaOH used per g of polyester	Molecular weight, from terminal group determination	Polydispersity coefficient M_v/M_t
1	0.0	0.119	4054	47.6	2100	1.93
2	3.0	0.110	3747	47.6	2100	1.78
3	6.0	0.102	3475	47.6	2100	1.66
4	9.0	0.097	3303	47.6	2100	1.57
5	14.0	0.078	2657	47.5	2100	1.26
6	20.0	0.078	2657	47.6	2100	1.26
7	35.0	0.076	2589	47.6	2100	1.23

Note: Molecular weight was calculated from terminal group content by the formula $M = \frac{100{,}000}{a}$, where a is ml of 0.02 N NaOH used per g of polyester.

TABLE 3

Properties of mixtures of polyesters

Amount of low molecular weight polyester, as % by wt.	Specific viscosity of a 0.5% solution in benzene	Molecular weight, from viscosity M_v	Ml 0.02 N alkali used in titration of terminal groups	Molecular weight, from terminal groups, M_t	Polydispersity coefficient M_v/M_t
0.0	0.194	6608	15.2	6579	1.004
0.5	0.193	6575	15.9	6289	1.04
3.0	0.190	6473	17.0	5882	1.10
7.5	0.183	6234	19.7	5076	1.22
15.0	0.174	5978	23.8	4223	1.42
25.0	0.164	5587	28.1	3558	1.57
50.0	0.145	4940	38.8	2577	1.66
75.0	0.130	4429	41.6	2403	1.84
100.0	0.120	4088	47.6	2100	1.95

The data of Table 3 confirm the previously expressed view that the polydispersity coefficient, which is the ratio of the molecular weights as derived from viscosity and terminal group determinations, respectively, may provide us with a useful measure of the polydispersity of the given polymer. As appears from Table 3, the polydispersity coefficient rises sharply with increase in the polydispersity of the given mixture. Fig. 2 shows graphically how the two molecular weights vary according to the content of one or the other polyester in the mixtures.

The mixtures were placed in tubes and heated for 35 hrs at 150° in an atmosphere of nitrogen. The tubes were allowed to cool, and were then opened and the contents were examined; the results are given in Table 4.

TABLE 4

Degradation of high-molecular polyester by the action of low-molecular polyester

Amount of low-molecular weight, polyester, as % by wt.	Specific viscosity of a 0.5% solution in benzene	Molecular weight, from viscosity M_v	Ml 0.02 N alkali used in titration of terminal groups	Molecular weight, from terminal groups M_t	Calculated molecular weight	Polydispersity coefficient M_v/M_t
0.0	0.194	6608	15.2	6579	–	–
0.5	0.166	5655	15.9	6289	6439	0.9
3.0	0.160	5451	17.1	5882	5854	0.92
7.5	0.144	4906	19.7	5076	5077	0.96
15.0	0.128	4360	23.7	4223	4280	1.03
25.0	0.115	3918	28.2	3558	3550	1.10
50.0	0.091	3100	38.8	2577	2717	1.20
75.0	0.086	2930	41.5	2403	2323	1.21
100.0	0.076	2589	47.6	2100	2108	1.23

NOTE: Molecular weight was calculated from the formula: $M = \frac{100 + q}{\frac{100}{M_0} - \frac{q}{M_1}}$.

Discussion of results. The experiments show that polyesters of different molecular weights react with each other when heated together, giving products having the mean molecular weight of the mixture. This process resembles that observed when polyesters are heated with dicarboxylic acids, as described by one of us and Golubev [8]. The process is of a degradative nature, as may readily be seen from an inspection of the curves of Fig.3, plotted from the data of Table 4.

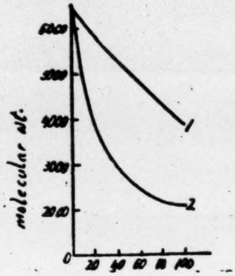


Fig. 2. 1) Change in molecular weight as calculated from viscosity; 2) change in molecular weight as calculated from terminal groups.

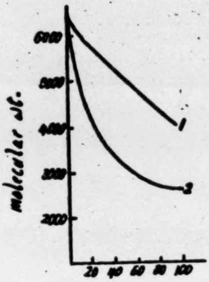


Fig. 3. 1) Change in molecular weight as calculated from viscosity, before heating; 2) change in molecular weight as calculated from viscosity, after heating.

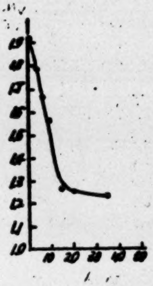


Fig. 4. Change in polydispersity coefficient with time.

We see from Fig. 3 that the fall in molecular weight of a mixture of two polyesters taking place after heating is much greater than would follow from the simple addition rule, showing that reaction must have taken place between the two polyesters. It may thus be concluded that degradation of the high-molecular by the low-molecular polyester does in fact take place. Fig. 4, which represents change in polydispersity coefficient during heating, shows that this reaction is one of degradation, and like all such processes, it leads to increase in homogeneity of the polyester.

As appears from Fig. 4, based on the data of Table 1, heating the polyester mixture leads to lowering of the molecular weight and of the polydispersity coefficient of the product. Similar effects are observed when we heat mixtures containing various proportions of low-molecular polyester, which in this case acts as the degradative agent. Fig. 3, which is based on the data of Table 4, illustrates the relation between change in molecular weight after heating mixtures of polyesters and the content of low-molecular polyester. Whereas Fig. 4 shows the rate of change of polydispersity with time, Fig. 5 represents change in polydispersity of the polyester after achievement of the equilibrium state, i.e., after completion of the degradative process. As appears from Fig.5, increase in the proportion of the low-molecular polyester favors the degradative process, and so leads to the formation of an increasingly monodisperse polyester.

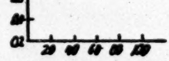


Fig. 5. 1) Change in coefficient of polydispersibility of polyester mixture before heating; 2) after heating.

Our results are of importance not only for the comprehension of the individual stages and steps of the process under consideration, but also for the understanding of certain general and basic aspects of the process of polycondensation, in general. An important consequence of this research is the establishment of the presence of exchange reactions proceeding between polyester molecules in the absence of the initial substrates. The existence of these exchange reactions is in the given case demonstrated by the reaction between two polyesters of differing molecular weight, but it should be supposed that it also takes place between polyesters of similar or even identical molecular weight. The present study has thus afforded additional confirmation of the existence of exchange reactions between growing molecules, proceeding without the agency of low-molecular initial substrates. Bearing in mind that the content of terminal groups falls rapidly with growth of the chains it will be obvious that such exchange reactions may be of importance both when they proceed at the expense of terminal groups and when they depend on reaction between ester bonds of different chains. This possibility has been envisaged by us in an earlier paper [5].

SUMMARY

1. A study of the exchange reaction between polyesters of different molecular weight shows that they react to give a single polyester.

2. The low-molecular polyester acts as a degradative agent with respect to the high-molecular ester.

3. The extent of degradation of the high-molecular polyester is proportional to the content of low-molecular polyester in the mixture.

4. The polydispersity coefficient falls during heating of polyester mixtures as a result of the degradative reaction.

5. A study of the kinetics of degradation of high-molecular polyesters when heated with low-molecular polyesters shows that the polydispersity coefficient falls regularly as the reaction proceeds.

6. A study has been made of the thermal degradation of polyesteri at various temperatures.

7. The exchange reaction is shown to be of considerable significance for the process of polycondensation.

Received April 4, 1952

Institute of Organic Chemistry
Academy of Sciences USSR

LITERATURE CITED

[1] V. V. Korshak and V. A. Zamyatina, Proc. Acad. Sci. USSR, 59, 909 (1948).

[2] V. V. Korshak and S. V. Vinogradova, Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 1, 63 (1951).

[3] V. V. Korshak and S. V. Vinogradova, Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 2, 179 (1952). *

[4] V. V. Korshak and S. V. Vinogradova, Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 1, 180 (1951).

[5] V. V. Korshak and S. V. Vinogradova, Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 3, 334 (1951).

[6] V. V. Korshak and S. V. Vinogradova, Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 6, 756 (1951).

[7] P. J. Flory, J. Am. Chem. Soc., 62, 2255 (1940).

[8] V. V. Korshak and V. V. Golubev, Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 4, 379 (1949).

[9] V. V. Korshak and S. R. Rafikov, Proc. Acad. Sci., 48, 36 (1945).

[10] V. V. Korshak and V. A. Zamyatina, Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 6, 609 (1945).

[11] V. V. Korshak and S. V. Vinogradova, Proc. Acad. Sci., 77, 277 (1951).

[12] V. V. Korshak and V. A. Zamyatina, Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 4, 412 (1948).

[13] S. R. Rafikov, V. V. Korshak, and G. N. Chelnokova, Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 6, 642 (1949).

[14] P. J. Flory, Chem. Rev., 39, 137 (1946).

[15] V. V. Korshak and S. V. Vinogradova, J. Gen. Chem., 22, 1176 (1952). **

---

* See Consultants Bureau English Translation, p. 193.

** See Consultants Bureau English Translation, p. 1225.

BLANK
PAGE

REMARKS ON "THE THEORY OF RESONANCE OR MESOMERISM"

Ya. K. Syrkin and M. E. Dyatkina

That work of genius of I. V. Stalin "Marxism and problems of linguistics which has brought about a veritable revolution in the domain of linguistics was an outstanding contribution to the theoretical superstructure of Marxism-Leninism. In the same way as over 40 years ago V. I. Lenin, in his work of genius "Materialism and Empiriocriticism", liberated the natural sciences from mysticism and Machism, Comrade Stalin's work on the problems of linguistics led Soviet linguistics out of the critical situation in which it had found itself, and freed it of the vulgarizing and mistaken "new teaching" of the science of language.

Having creatively developed and enriched Marxist-Leninist theory with its new discoveries and propositions, I. V. Stalin's work has pointed the way towards further development and achievement of all domains of Soviet science. At the same time, this work has dealt a decisive blow to idealism, metaphysics, and reactionary ideology. Stalin's memorable words, that "no science can develop and flourish without a clash of ideas, without free criticism" have become the motto of those engaged in creative science. This proposition establishes a new and important dialectic law governing the motive force of our development, which is criticism and self-criticism. Comrade Stalin's work "Marxism and the problems of linguistics" teaches all those who are active in Soviet culture how to apply veritable partisanship to science, this partisanship being diametrically opposed to bourgeois objectivism. At the same time, veritable partisanship in no way rejects a really objective analysis of natural phenomena, inasmuch as really scientific, objective explanations of the laws governing the world of reality are always and in every case found to confirm the correctness of dialectic materialism..

In view of I. V. Stalin's brilliant treatise "Marxism and the problems of linguistics", and of the historic resolutions of the Central Committee of the All-Union Communist Party on the problems of ideological work, we should adopt a critical attitude to the results of our earlier researches, and we should reconstruct our scientific work on the basis of the creative application of Marxist-Leninist theory. The absence of the creative application of the laws of materialistic dialectics to particular domains of knowledge leads to conclusions which are in contradiction to true science, and to pseudo-scientific theories. One example which confirms the truth of this proposition is the profoundly erroneous "resonance theory", which was, to their great regret, for a long time supported by the authors of this paper. A critical survey of our earlier papers connected with the "resonance theory", together with their analysis in the light of Marxist-Leninist teaching, leads us to the conclusion that the reason for our errors was that we did not, in our research work, creatively apply the principles of dialectical materialism, we did not adopt a critical attitude towards the quasi-scientific ideas of the moribund culture of the capitalistic West, and we did not appraise at its true value the progressive significance of the materialistic theory of chemical structure, of which the creator was that classical figure of Russian natural science, A. M. Butlerov.

During the course of the discussions which took place in June 1951 we acknowledged the mistaken nature of the "resonance theory", and the erroneous nature of those of our papers in which we made use of this theory, or supported it. In this connection we consider it to be necessary to dwell on the problems and the role of Russian science in creating the theory of chemical structure, and on the significance of Butlerov's ideas for the whole of the later development which took place in this domain, as well as on the methodological origins of the errors of the "resonance theory", and on the chemical absurdities of this "theory". The basic error of our book "The chemical bond and the structure of molecules" was the absence of an historical approach to the development of the problem of the structure of chemical compounds. This led us to present a distorted picture of the real position of the given problem, and to an erroneous presentation of the principles on which are based modern conceptions of the structure of molecules. The theory of the structure of organic compounds, from which are derived present-day achievements of this branch of chemistry, stems from the work of Butlerov in the eighteen-sixties. Before then, as Butlerov said, organic chemistry was distinguished by the way in which experiment outdistanced theory. A great number of experimental facts had been accumulated, but there was no general idea, no general approach, which would allow of all this material being considered from a single viewpoint.

Many scientists, such as, for example, Kekule, held eclectic views, and did not appreciate the role of theory, not believing in the possibility of creating a unifying theory which could serve as a basis for the whole of organic chemistry. Kekule, Kolbe, and others believed that it was impossible to visualize the way in which mutual bonds between atoms in molecules exist. Agnosticism also typified the views of Gerard, who held that chemical methods may permit us to gain knowledge of the past or the future of molecules, but not of their present.

Under these conditions Butlerov's theory of chemical structure initiated an absolutely new period in the development of chemistry. It was from that time, i.e., after Butlerov had made his fundamental contributions, that the idea of chemical structure as the factor determining the chemical behavior of substances entered into chemistry. The exposition of modern theories of the structure of molecules must necessarily begin with an account of this period, as that of the beginnings of the science of chemical structure. Our very grave error was that we did not take into account the historical approach to the problem, that we treated its present state without reference to its historical development, and that we presented it as if our knowledge of the structure of molecules dated from the time when the quantum mechanics methods were applied to the estimation of the energy and of other properties of molecules.

In actual fact, the basis of modern views, and their origins, are those concepts of molecular structure which had been developed by Butlerov. An insufficient appreciation of the role of Butlerov and of his theory of chemical structure was the cause of the errors of our book. This theory, which lies at the basis of our modern concepts, was in effect thrown out of our book. Our mistake was that we reduced all the richness and the importance of the theory only to the dashes representing valency, and then wrote that the structural theory is a formal one.

In actual fact, Butlerov's theory of chemical structure contained profound ideas, which for long years determined the development of the whole of organic chemistry. The basic proposition of the theory of structure is the concept of the presence in each molecule of a definite order of atomic bonds, which are represented as structural formulas; it reflects the fact that a molecule is a qualitatively determined particle, possessing a unique and definite structure for each molecule. This is a profoundly materialistic idea, without which all the later development of the theory of structure would have been impossible. It is to Butlerov, who established the reality of the chemical structure of molecules that we owe the concept that the chemical behavior of substances is determined by their chemical structure.

Butlerov's formulation of the idea of chemical structure differs radically from the views of Kekule, or Cooper, who considered structural formulas to be only reaction formulas, "transformation formulas". Thus the real author of the theory of structure is incontestably A. M. Butlerov.

All these circumstances were not presented in our book. We should also emphasize that the concept of chemical structure introduced by Butlerov is by no means confined only to the questions of location of atoms and distribution of bonds in a molecule.

One of the foundation stones of Butlerov's theory is the teaching about the mutual influence, the mutual action on each other of atoms, both directly combined and not combined.

According to Butlerov, chemical structure is the "distribution of the action of chemical forces (affinities), owing to which chemical atoms, by acting directly or indirectly on each other, combine to give chemical molecules".

In scientific matters Butlerov opposed, from a materialistic standpoint, scientific idealism which rejected the actual existence of atoms in molecules; he opposed creeping empiricism, which degraded the role of theory in science.

On the other hand, Butlerov's materialistic theory resulted from the acknowledgement of the reality of atoms and from a scientific conviction that it would be possible to study their properties. It is in this approach of Butlerov's that the materialistic tendency of Russian natural science was displayed. It is thanks to this that Butlerov's theory correctly depicts the basic features of the chemical form of the movement of matter.

Special mention should be made of the great significance of Butlerov's contribution to the question of the role of theory in scientific research. The predictive power of his theory stimulated a whole series of new discoveries. The impeccable theoretical argumentation and experimental confirmation characteristic of Butlerov's work are an illustration of unity of theory and practice. To this is ascribable the vitality of Butlerov's teaching on chemical structure.

We should note that Butlerov applied his theory of structure to the prediction of a number of compounds which were as yet unknown, and which he then synthesized, such as, for example, the tertiary alcohols. Butlerov also explained isomerism, and gave a correct theory of tautomerism. It should also be pointed out that Markovnikov, by making use of the concepts of reciprocal action on each other of atoms, was able to formulate his well-known rule for reactions of addition, substitution, and splitting off. This rule is a manifestation of the general laws of mutual influence of atoms and groups of atoms in molecules, and it is still today fully valid.

Butlerov's dynamic concept of the molecule was a brilliant anticipation of modern views of the nature of the molecule, as a complex dynamic system. It was this materialistic principle, characteristic of Russian science, which we should have emphasized, inasmuch as it was Butlerov's strength in his struggle against idealists and agnostics. One of the mistakes of our book, due to our disregard of general philosophical principles, was that we did not base our views on Butlerov's materialistic theory, from which alone could the study of the structure of molecules be developed. The absence of Butlerov's theory from our book was the reason why it became permeated with idealistic and mechanistic concepts. We should also have emphasized that our present-day views on the structure of atoms and molecules are based on M. V. Lomonosov's atomistic concept and on D. I. Mendeleev's periodic table. The over-estimation of second-rate work by foreign authors, and the under-estimation of the work of Soviet scientists were connected with the under-estimation of Butlerov's theory.

A serious shortcoming of our book is that it pays no attention to questions of methodology. In dealing with the theory of the chemical bond we did not take into account that this problem is directly concerned with the general philosophical and methodological problems of chemistry and physics. Actually, as is evidenced by a whole series of declarations made in the scientific press and at discussion meetings devoted to the theory of chemical structure, the very enunciation of the problem of the nature of the chemical bond involves the struggle between idealism and materialism. On the one hand we have the materialistic concept of the molecule as an objective reality, and on the other the pragmatic, agnostic approach, connected with the idealistic view of the unknowability of the molecule. In the latter case objective criteria of the reality of the molecule and of the chemical bond disappear. In our exposition of the problem of the nature of the chemical bond we did not consider methodological questions, and we did not criticize idealistic presentations.

Physical idealism and mathematical fetichism have largely infiltrated into chemistry in the form of the "resonance or mesomerism theory". The resonance theory derives from a formally incorrect interpretation of one of the approximative methods of quantum chemistry—the method of localized pairs. The sense of a definite chemical structure was ascribed to the individual terms of the sum approximately expressing the wave function describing the state of the molecule. In reality, the individual terms making up the wave function used as a first approximation possess only a purely mathematical significance, and are not connected with the real properties of objectively existing molecules. This incorrect interpretation led us to an erroneous concept of allegedly existing physical phenomena, viz., quantum-mechanical resonance structures, according to which superposition of resonance structures determines the real state of the molecule. We were in error in uncritically accepting this concept, and in applying it widely in our book, in which we frequently used such expressions as "is explained by resonance", "ascribable to presence of structures", or "ascribable to appearance of structures". Explanations based on the use of nonexistent structures must, of course, be erroneous, for since they are merely terms of a mathematical expression the individual terms of the development of a wave function cannot be the causes of physical effects. Such objectivization of a purely mathematical concept must be considered to be physical idealism. The resonance theory was an idealistic interpretation of the approximative method of localization of pairs. Other manifestations of this objectivization were such expressions as "structures co-exist in molecules" or "structures are represented", which might mislead one into thinking that real structures are intended. A mistaken belief in the existence of fictitious structures led us to a mistaken understanding of resonance as a phenomenon. The objective reality of a concrete form of motion of matter which determines the properties of actually existing states of molecules, independent of our consciousness of them, has been replaced in the resonance theory by purely speculative and subjective structures, having no real existence. Thereby objective reality was replaced by fictitious representations, and this is a manifestation of idealism in science.

We did not in our book subject the resonance theory to criticism from a philosophical angle, and we thus did not discern the Machist tendencies of its authors. Yet this should have been done, the more so as the authors of the "resonance theory" themselves treat resonance as a speculative concept, as a "convenient" descriptive method, for this reason accepted as correct; as we have seen, this is unconcealed Machism. The harm done to the natural sciences by concepts of this sort has been pointed out by V. I. Lenin in his work of genius "Materialism and Empiriocriticism", in which he showed that the principle of economy, which is fundamental to the theory of cognition, must inevitably lead to subjective idealism. The multiplicity of structures inherent in the resonance theory is a deviation from the materialistic concept of Butlerov, and is a retrograde step towards the pre-Butlerov agnosticism of Gerard, Kekule, and others.

The resonance theory, being an erroneous interpretation of one of the approximative methods of calculation applied to multi-electronic systems, does not derive from quantum mechanics. The difficulty of approach to such complex systems lies in the fact that we do not know their real wave functions, describing the state of the system. For this reason, in the approximative methods known to us today, one of which is the method of electron pairs, or of valency schemes, the actual wave function is given approximately by certain mathematical expressions, which only very crudely reflect the nature of the actual wave function. It should here be pointed out that there may be various ways of approximating to a correct wave function. In quantum chemistry, in addition to linear combinations of derivatives of monoelectronic wave functions, used in the method of electron pairs, other mathematical approximations to the correct wave function are applied. Thus for a large number of problems the method of molecular orbits is used, based on a different approximation, which is in no way connected with "resonance structures". Other approaches are also possible, which do not necessarily make use of linear combinations of simpler functions. As an example of this, we would point out that in making calculations for the hydrogen molecule, which allowed of the calculation of the energy of formation of this molecule with a high degree of accuracy, use was made, as an approximative wave function, of an expression not based on a linear combination of monoelectronic functions. Thus we see that the use of linear combinations of derivatives of mono-electronic functions is only one of the particular and imperfect ways of arriving at an approximation to the correct wave function.

Resonance structures were made use of in the "resonance theory" as if they were ordinary structural formulas. Yet it should be realized that the individual terms of which the wave function is made up, in the method of electron pairs, are not connected with any experimentally observable physical data whatsoever. A physical sense is possessed only by the wave function itself, as a whole, being directly related to real physical characteristics of objectively existing molecules, such as the energy of molecules, the distribution within them of electric charges, etc.

Our mistake was that we did not give a clear-cut explanation, in the above sense, of the individual terms when dealing with wave functions, and that when we considered them separately from the particular mathematical operations to which they belonged we tended to regard them as if they were of the nature of primary factors, determining the actual physical properties of the molecule. This was an unjustifiable use of the individual components of a wave function: we raised them to the level of an absolute, independent of matter. The elevation of individual items of cognition to the rank of absolutes was, as we know, described by Lenin as being philosophical idealism: "from the view point of dialectical materialism philosophical idealism is a one-sided, exaggerated . . . hypertrophy (expansion, inflation) of one of the features, aspects, or facets of cognition into an absolute, detached from matter or from Nature, a deification".*

There is no trace of rationality in treating of individual terms of an analysis as objectively existing resonance structures. The posing of the imaginary problem of establishing experimentally the existence of separate "resonance structures" is a misunderstanding.

We, unfortunately, added to the methodological errors of the "resonance theory" by introducing the concept of transitional structures. On the grounds that the density of the electron cloud is expressed as the square of the wave function, and is thus represented in the form of the sum of the squares of the individual terms of the analysis and of their double derivatives, we connected the expression for the latter with separate "transitional structures". As a result, the individual terms of the sum, which are of purely mathematical origin, became objectivized, and were regarded as factors determining the properties of real molecules. In this case, too, a fictitious, imaginary picture was elevated to the status of a factor determining objectively real phenomena.

We did not in our book clearly differentiate between the concepts of state and structure, and this was one of the causes of our mistaken interpretation of individual components of the approximative wave function, insofar as we regarded these individual terms as separate states of the system, whereas in reality these terms of a mathematical expression do not relate to any states whatsoever which could exist in a molecule, i.e., they have no real physical sense.

It should be noted that a justified criticism of the "resonance theory" does not contradict the value of quantum-chemical calculations based on existing methods. These calculations are very rough and imperfect ones. It is essentially a zero approximation, but it can in a number of cases be useful, as, for example, in comparing different molecules with conjugated bonds, or molecules with different kinds of annelation of benzene rings (acene, phene), etc. The existing methods permit of the very approximate calculation of the total energy of π-bonds for the basal and the excited states. The final values derived for total energy are in no way connected with any reference to separate "resonance" structures. As for the quantum-mechanical method of molecular orbits, this has no connection at all with "separate structures", and it can find application in a limited range of problems (comparison of molecules with conjugated bonds). To this category belongs the calculation of transition from the singlet to the triplet, bi-radical state, etc.

---

* V. I. Lenin. Philosophical Notes, Gospolitizdat, 1947, p. 330.

The basic shortcoming of known quantum-chemical methods used in our work is their lack of precision. For this reason, where large effects of the order of tens or even hundreds of kg-calories are concerned, these methods, and particularly methods of molecular orbits, may be applied for comparative purposes. It should be borne in mind that because of their imprecision and approximative nature the applicability of these methods is very restricted. It should also be noted that although the application of quantum mechanics to chemistry may be of value for the provision of data relating to individual characteristic molecules, this approach cannot lead to the elucidation of the whole complex and specification of chemical phenomena. The further development of the theory of chemical structure should be based on synthesis of organic substances followed by a study of their reactivity and other chemical properties, in relation to their structure. Quantum-chemical methods can be of only auxiliary value in this study. Special caution must be exercized in applying the results obtained by quantum-chemical calculations for simple molecules to more complex ones; the result should always be checked by the data of chemical experimentation.

Inasmuch as the individual components of wave functions are not related to any experimentally observed real characteristics of molecules it is natural that the resonance structures considered cannot serve for the drawing of any conclusions relating to the objective properties of molecules. To this are due the mistakes made in the application of the "resonance theory" to chemistry. Explanations based on the use of resonance structures are only apparent ones, for, being a consequence of the incorrect interpretation of a method of calculation, the concept of resonance cannot give satisfactory explanations of chemical and physical facts. Our mistake was that we did not discern the nature of the "explanations" afforded by the "resonance theory", and that we made wide use of these "explanations". The application of resonance structures to the explanation of experimental facts opened up the way for arbitrary reasoning, inasmuch as the impression was created that explanations could be possible where in fact there was no explanation.

Resonance structures are used in the "resonance theory" for the explanation of experimental results. The first consequence of this is that the way is opened for finding "explanations" of experimental errors. Thus, for example, erroneous experimental data relating to the alleged increased distance between two methylene groups in dibenzyl were easily explained as being a consequence of the tendency of dibenzyl to break up into two tolyl radicals, owing to which the distance between the methylene groups is lengthened. Later experiments, however, showed that the distance in question is shortened, not lengthened. In the same way erroneous spectrometric data were explained by "proving" that the benzoyl ion causes an electron shift in the ring, and is an ortho-para orientator. This was readily accomplished by representing the structure of benzoic acid with a valency link between the two oxygens of the carboxyl group, as a result of which the negative charge was shifted to the ortho position of the ring. Later work showed, however, that the experimental data for which the explanation was given were erroneous. It was thus always possible to find any fictitious "structure" whatsoever, and to believe that nothing else needed to be done. The possibility then appeared of explaining complex, and at first sight inexplicable, facts by means of structures invented ad hoc to suit each case. For example, the shortened interatomic distances of organic fluorine derivatives were explained by ascribing to fluorine a bivalent state with a positive charge. Thus, specially for this given case, fluorine, that most electronegative of all the elements of Mendeleev's periodic table, becomes electropositive and bivalent. In this way apparent explanations were fabricated.

To the same category of errors belong explanations involving the reduction of chemical problems to structures or to the matching of structures with ordinary and stretched bonds. Formal schemes not conveying the real state of molecules are used in the "resonance theory" for writing structures. The possibility of improvising one or another structure thus arises, and not infrequently mutually exclusive assumptions are made from case to case. Thus, for example, for the explanation of the normal value of the moments of triphenyl-, fluoro-, chloro-, bromo, and iodo-methane it is necessary to assume hindrance of the shift of negative charges from the benzene rings to the electronegative halogens. But for the high dipole moment of nitrobenzene as compared with nitromethane it is assumed, on the contrary, that the shift of negative charges to the electronegative oxygen atoms of the nitro-group is facilitated. In this way the possibility of providing explanations for everything is furnished; such explanations cannot but be thought to be unsatisfactory.

The errors pointed out above, relating to the structure of molecules, also affected problems of reactivity as applied to molecules during reactions. According to how the reaction went this was said to be due to the molecules "reacting in one or another resonance form". This gave rise to erroneous views on the mechanism of a large number of organic reactions.

The procedure adopted, instead of making a critical examination of the reaction mechanism, was to write some resonance structure appropriate to the way the given reaction proceeded and to the nature of the end product, or arrows were appropriately distributed about the formula. It should be noted that our errors also apply to the mesomerism theory, to the same degree as to the "resonance theory". Every resonance structure may be represented by the aid of arrows.

Instead of establishing the real reaction mechanism (by means of kinetic measurements, by the method of labelled atoms, etc), the "theory of resonance or mesomerism" replaces the reaction process and its laws by selected structures or arrows, which are made to fit the results obtained by the use of unproven hypothetical ions, both positively and negatively charged, carbonium and carbanium ions, and a host of others which figure in the literature, and for whose existence there is often very little evidence. We did not, to our regret, expose these errors of the "resonance or mesomerism theory" as applied to reactivity, and the same mistaken acceptance of the theory is to be found in the work of a number of authors who gave theoretical explanations of experimental results in organic chemistry.

The "resonance or mesomerism theory" by giving baseless explanations of reaction mechanisms created an atmosphere of contentment with the apparently adequate theoretical basis provided for organic chemistry. Here, too, we were in error.

To summarize what we have said above, we have come to the conclusion that the "resonance or mesomerism theory" is one of the manifestations of idealism in science. It gives expression to bourgeois ideology in chemistry, in the same way as bourgeois ideology has infiltrated into other domains of science, on which creative discussion meetings have been held during recent years.

The sources of our mistakes were:

1. We were not sufficiently guided in our work by the principles of materialistic dialectics, which alone reflect the objective processes of the real world and its laws.

2. The absence of criticism and of verification of the scientific coherence of the theory of the chemical bond from the stand-point of dialectic materialism.

3. The under-estimation of the significance of the materialistic trend of the classical workers of Russian natural science, of their patriotism, and of their contributions to science.

4. An uncritical attitude towards the reactionary ideas of certain Western scientists, which are symptomatic of the decay of the moribund culture of capitalism.

5. An uncritical attitude towards the interpretation of the numerical results given by the approximative quantum-mechanical methods.

We shall in our future work make every effort towards the rectification of our mistakes. Our future task will be to contribute to the development of knowledge of the structure of molecules on the lines of the teachings of dialectical materialism and of the ideas of Butlerov, Mendeleev, Markovnikov, and other coryphei of Russian science.

It is necessary to make the widest possible use of the scientific heritage of Butlerov, and, basing ourselves on his first propositions in the domain of the theory of chemical structure, to generalize the material since accumulated so as further to develop the theory of chemical structure with the help of the achievements of quantum mechanics.

The essential problem to which attention should be directed is that of the connection between chemical structure of molecules and their reactivity. This work should be conducted by means of studies of the kinetics of the reaction, and by the use of labelled atoms, with the object of elucidating reaction mechanism, estimating the strength of bonds, their equivalence or non-equivalence, elucidating the question of the part played by radicals, ions, and other intermediate products in chemical reactions, and of investigating the role of the solvent in chemical processes. The elucidation of the role of thermodynamic and kinetic factors in determining the course of chemical reactions is also of importance.

A second approach to be used in our work in this domain should be the further experimental study of the physical properties of molecules, and in particular of their polarity, by measurements of dipole moments, of the magnetic properties of chemical compounds, with the object of elucidating the valency state of the atoms, and the types of bonds between them, and of their optical properties. The object of work in this direction should be to obtain data on the structure of molecules and to elucidate the nature of the reciprocal effects between atoms and groups in molecules.

One of the tasks before us is the application of the methods of quantum chemistry to the solution of particular problems connected with the mutual effects on each other of atoms in molecules, as an approach to the problem of the interaction of σ- and π-bonds and to the question of directional valencies and valency states of atoms. At the same time we believe that the existing methods of quantum chemistry can, in view of their very approximative nature, have only a very limited sphere of applicability, and need to be perfected.

It is necessary, in the domains of reactivity, structure, and the study of the physical properties of molecules, to explore those problems which would be of help in solving the practical problems which confront chemical industry.

BLANK
PAGE

FREE ENERGY AND HEAT OF DEHYDRATION OF CRYSTAL-HYDRATES OF URANYL NITRATE AND CHLORIDE

A. F. Kapustinsky and L. I. Baranova

There are no published data relating to the free energy of dehydration of crystal hydrates of uranyl salts, and only a very few measurements have been made of heats of hydration of a few uranyl salts, by the calorimetric method [1]. We shall in this paper present the results of tensimetric determinations of the dissociation pressure of uranyl nitrate hexahydrate and uranyl chloride trihydrate at various temperatures, from which the free energy and the thermal effects of the reaction may be derived.

A tensimeter of the Frowein type was used, in which the number of ground joints was reduced, but their dimensions were increased, and mercury seals were introduced. The experimental and the standard substances were placed in bulbs a and b of the tensimeter (Fig. 1), and the bulbs were connected by the joints d and e, fitted with mercury seals, to a differential mercury manometer, on one limb of which was a bulb c which served as a reservoir for the mercury when the manometer was held in a horizontal position during evacuation. A large vacuum tap k separated the instrument from a steam trap and an oil pump giving a vacuum of 0.01 mm. Vacuum grease was used for the taps and joints, and redistilled mercury was taken for the manometer.

The instrument did not leak for several days at 55°.

The tensimeter was immersed in a water thermostat provided with a window, a toluene thermoregulator, and an electronic relay; the temperatures used were 25° + 0.005° and 50° + 0.05°. The constancy of temperature was checked with the aid of a Beckman thermometer, and temperatures were read on a normal thermometer graduated in 0.1°, calibrated at VIMS.* Pressure was read with the aid of a microscope-vernier with a nonius checked against a standard, the accuracy of reading being 0.1-0.05 mm. The reference substances taken were water and sulfuric acid of a concentration giving a water vapor pressure of 0.008 mm. The ordinary conditions necessary for tensimetry were observed. The results were checked by measurements of the dissociation pressure of crystal hydrates of copper sulfate, which can readily be obtained pure, and which have been extensively studied.

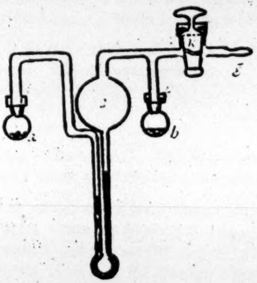


Fig. 1. Diagram of tensimeter.

We approached each equilibrium from both sides (with rising and with falling temperature). The time taken for establishment of equilibrium was different for different crystal hydrates, being of the order of minutes for hexahydrate, 60-70 hr for the trihydrate of uranyl nitrate, and 30-40 hr for the trihydrate of uranyl chloride. Well reproducible results were obtained for all the salts. Each value recorded for the dissociation pressures is the mean of a least two measurements differing by not more than 1%.

The salts were prepared from chemically pure specimens from the Mendeleev Institute collection. Uranyl nitrate hexahydrate was recrystallized four times, after which it was analyzed by precipitation with ammonia according to Hillebrand, and was found to contain 5.8 molecules of water. The powdered crystals were kept in a vacuum desiccator over 35% sulfuric acid, to constant weight. The trihydrate was prepared by keeping the hexahydrate over 65% sulfuric acid for 4 weeks, constant weight being achieved after the loss of 2.94 mol of water. The trihydrate of uranyl chloride was prepared similarly. Lewenstein [2] has confirmed earlier work showing the existence of these hydrates, giving the intervals of concentration of sulfuric acid corresponding with the equilibrium points of the appropriate crystal hydrates.

It is known [3] that as a result of the hydrolysis of uranyl chloride by its own water of crystallization at temperatures above 90° hydrogen chloride is evolved. We performed special experiments with the object of finding out whether this hydrolytic reaction takes place at the highest temperatures used by us, viz., 50°: dry air was passed at a rate of 10 liter/hr through uranyl chloride hydrate, and then through silver nitrate solution, for several hours. The solution became opalescent, although no precipitate was formed. This result corresponds with a dissociation pressure (with evolution of hydrogen chloride) of the order of 10^{-7} mm, i.e., hydrolytic decomposition of the salt is practically absent at temperatures below 50°. The specimen of uranyl chloride trihydrate was twice recrystallized, and was then kept in a vacuum desiccator over 65% sulfuric acid; its purity was checked by analyzing it by Hecht and Danau's hydroxyquinoline method. The results obtained are presented in Table 1.

---

* All-Union Institute of Mineral Raw Materials.

TABLE 1

A. System:
$UO_2(NO_3)_2 \cdot 6H_2O \rightleftarrows UO_2(NO_3)_2 \cdot 3H_2O + 3H_2O$ (vapor)

Temperature, °C	25	30	35	40
Vapor pressure of water vapor, mm	7.1	10.3	14.8	21.3

B. System:
$UO_2Cl_2 \cdot 3H_2O \rightleftarrows UO_2Cl_2 \cdot H_2O + 2H_2O$ (vapor)

Temperature, °C	35	40	45	50
Vapor pressure of water vapor, mm	2.1	3.1	4.8	6.7

The results are in good agreement with a linear relationship between log p and 1/T. The curves of Figs. 2 and 3 are constructed by the method of least squares, for the systems A and B. The equations of the curves are

$$\text{(A)} \quad \log p = -\frac{2949}{T} + 10.74. \qquad (1)$$

$$\text{(B)} \quad \log p = -\frac{3157}{T} + 10.58 \qquad (2)$$

and from them may be derived the standard heats and free energies of hydration. For system (A) $\Delta H = -13.49$ kcal and $\Delta F = -8.3$ kcal, while for system (B) $\Delta H = -14.44$ kcal and $\Delta F = -7.2$ kcal (at 35°).

As for the system uranyl nitrate trihydrate − dihydrate and water, the results obtained were much less reproducible. The relevant equation:

$$\log p = -\frac{2896}{T} + 9.87 \qquad (3)$$

gives $\Delta H_{298} = -13.3$ kcal. This value, as well as that for free energy (−0.8), must, however, be regarded as no more than a rough approximation, for which reason they are inserted in parentheses in Table 2.

Our values are in good agreement with published figures, derived from calorimetric measurements of heats of dissolution. Thus for system (A) $\Delta H_{298} = -13.0$ kcal according to de Forcrand [4], −12.92 kcal. according to Katzin, Simon, and Ferraro [5], and −13.49 kcal according to us, and for the system trihydrate − dihydrate and water, for the same salt, the thermal effect is −13.8 kcal according to de Forcrand, −14.2 kcal according to Katzin, Simon and Ferraro, and −13.3 kcal according to us. We have been unable to trace any published studies on uranyl chloride.

TABLE 2

Reaction	Heat and free energy, kcal	
	ΔH_{298}	ΔF_{298}
$UO_2(NO_3)_2 \cdot 6H_2O \rightleftarrows UO_2(NO_3)_2 \cdot 3H_2O + 3H_2O$	−13.49	−8.3
$UO_2(NO_3)_2 \cdot 3H_2O \rightleftarrows UO_2(NO_3)_2 \cdot 2H_2O + H_2O$	(−13.3)	(−0.8)
$UO_2Cl_2 \cdot 3H_2O \rightleftarrows UO_2Cl_2 \cdot H_2O + 2H_2O$	−14.44	−7.2 (at 35°)

LITERATURE CITED

[1] E. V. Britske, A. F. Kapustinsky, B. K. Veselovsky, L. M. Shamovsky, L. G. Chentsova, and B. I. Anvayer. Thermal constants of inorganic substances. Acad. Sci. USSR Publ., 1949; F. Rossini et al, Selected Values of Chem. thermodyn. properties, Bureau of Standards USA, 1952.

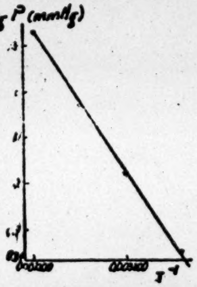


Fig. 2. Relation between the logarithm of the dissociation pressure of uranyl nitrate hexahydrate and 1/T.

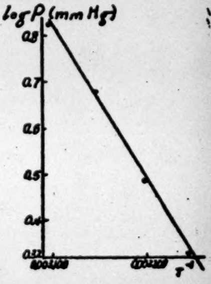


Fig. 3. Relation between the logarithm of the dissociation pressure of uranyl nitrate hexahydrate and 1/T.

[2] S. Lewenstein, Z. allg. anorg. Chem., 63, 69 (1909).

[3] Gmelin's Handbuch der anorganischen Chemie.

[4] de Forcrand, Comptes. rend. 152, 1073 (1911).

[5] L. Katzin, D. Simon, J. Ferraro, J. Am. Chem. Soc., 74, 1191 (1952).

Received July 1, 1952

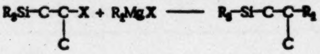
D. I. Mendeleev Institute of Technology

BLANK
PAGE

SYNTHESIS OF SILICOHYDROCARBONS FROM β-SILICOHALIDES AND ALKYL-LITHIUM

A. D. Petrov and V. P. Lavrishchev

Petrov and Mironov [1] have shown that in the syntheses of silicohydrocarbons by the condensation of secondary β-silicohalides with Grignard reagents:



$$R_3Si{-}C{-}\underset{C}{\underset{|}{C}}{-}X + R_1MgX \longrightarrow R_3{-}Si{-}C{-}\underset{C}{\underset{|}{C}}{-}R_1$$

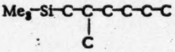
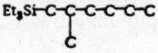
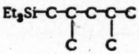
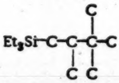
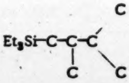
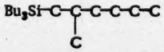
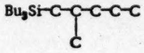
where R_1 is Et or Pr, the yields rise with increase in the length of the radicals R from Me to Bu.

We undertook the study of the condensation of secondary β-silico-halides with Grignard reagents containing radicals R_1 likely to give rise to steric hindrance, such as n-C_4H_9, iso-C_4H_9, iso-C_3H_7, and tert. C_4H_9.

Our experiments showed that much lower yields are obtained with these reagents, falling to zero for tert. C_4H_9. There are numerous indications in the literature that in the synthesis of silicohydrocarbons from silicohalides with the halogen attached to the silicon atom much higher yields are obtained when alkyl-lithium is used instead of Grignard reagent [2].

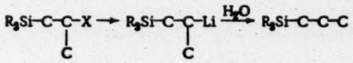
It was thought to be of interest to find out whether a similar effect is obtained when β-silicohalides are taken. As appears from Table 1 this was found to be the case. Not only does the substitution of lithium for Grignard reagents raise the yields by as much as 3-6 times, but it also allows of the introduction of such sterically difficult radicals as is tertiary butyl. The use of alkyl-lithium instead of Grignard reagents also affects the nature of the by-products of the reaction.

TABLE 1

Condensation product	Yield as % of $R_3Si{-}C{-}C{=}C$ taken	
	R_1MgX	R_1Li
 $Me_3{-}Si{-}C{-}\underset{C}{\underset{|}{C}}{-}C{-}C{-}C{-}C$	0.6	21.8
 $Et_3Si{-}C{-}\underset{C}{\underset{|}{C}}{-}C{-}C{-}C{-}C$	9	27
 $Et_3Si{-}C{-}\underset{C}{\underset{|}{C}}{-}C{-}\underset{C}{\underset{|}{C}}{-}C$	3.6	26
 $Et_3Si{-}C{-}\underset{C}{\underset{|}{C}}{-}\overset{C}{\overset{|}{\underset{C}{\underset{|}{C}}}}{-}C$	0	6.1
 $Et_3Si{-}C{-}\underset{C}{\underset{|}{C}}{-}C{<}^{C}_{C}$	17.4	-
 $Bu_3Si{-}C{-}\underset{C}{\underset{|}{C}}{-}C{-}C{-}C{-}C$	4	20
 $Bu_3Si{-}C{-}\underset{C}{\underset{|}{C}}{-}C{-}C{-}C$	-	18

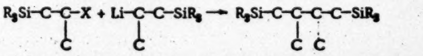
The side reactions taking place with alkyl-lithiums are:

1. Reduction of β-silane halides, as follows:



$$R_3Si{-}C{-}\underset{C}{\underset{|}{C}}{-}X \longrightarrow R_3Si{-}C{-}\underset{C}{\underset{|}{C}}{-}Li \xrightarrow{H_2O} R_3Si{-}C{-}C{-}C$$

2. Condensation, as follows:



$$R_3Si{-}C{-}\underset{C}{\underset{|}{C}}{-}X + Li{-}\underset{C}{\underset{|}{C}}{-}C{-}SiR_3 \longrightarrow R_3Si{-}C{-}\underset{C}{\underset{|}{C}}{-}\underset{C}{\underset{|}{C}}{-}C{-}SiR_3$$

Compounds of the type R_3SiR_1, which are the chief product of β-decomposition, were not found, showing that if this takes place at all it must be to a smaller extent than with R_1MgX. The main products were obtained in yields of 20-27%, and the by-products in yields of 8-12%. Where low yields of product were obtained, such as 6% with tert. butyl lithium, the yield of by-products rose to 33%.

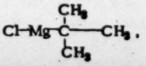
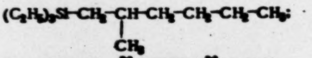
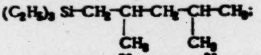
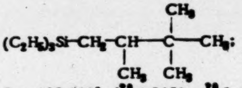
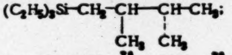
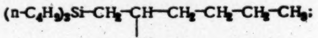
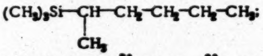
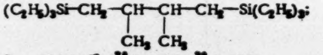
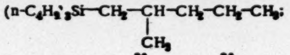
It is of interest that in the condensation of triethyl-β-bromopropylsilane with  $Cl{-}Mg{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CH_3$, where tert. butyl did not enter into the reaction of condensation, and where triethyl-tert.-butylsilane could also not be obtained, the reduction product, triethylpropylsilane, was obtained in 11% yield, and the product of condensation of the silyl halide, 1,4-di-(triethylsilyl)-2,3-dimethylbutane, in 6% yield.

TABLE 2

 $(C_2H_5)_3Si{-}CH_2{-}\underset{CH_3}{CH}{-}CH_2{-}CH_2{-}CH_2{-}CH_3$; B.p. 236-228°; d_4^{20} 0.7959; n_D^{20} 1.4448	Found %: C 72.72; 72.52; H 13,62; 13.48; Si 12.81; 13.55 $C_{13}H_{30}Si$. Calculated %: C 72.8; H 14.1; Si 13.1
 $(C_2H_5)_3\,Si{-}CH_2{-}\underset{CH_3}{CH}{-}CH_2{-}\underset{CH_3}{CH}{-}CH_3$; B.p. 233-234°; d_4^{20} 0.7979; n_D^{20} 1.4454	
 $(C_2H_5)_3Si{-}CH_2{-}\underset{CH_3}{CH}{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CH_3$; B.p. 229-230°; d_4^{20} 0.8050; n_D^{20} 1.4492	
 $(C_2H_5)_3Si{-}CH_2{-}\underset{CH_3}{CH}{-}\underset{CH_3}{CH}{-}CH_3$; B.p. 221-222°; d_4^{20} 0.7993; n_D^{20} 1.4460	Found %: C 72.5; 72.54; H 14.2; 13.92; Si 13.5; 13.62 $C_{12}H_{28}Si$. Calculated %: C 72.0; H 14.0; Si 14.0
 $(n\text{-}C_4H_9)_3Si{-}CH_2{-}\underset{CH_3}{CH}{-}CH_2{-}CH_2{-}CH_2{-}CH_3$; B.p. 306-306.5°; d_4^{20} 0.8054; n_D^{20} 1.4512	Found %: Si 10.67; 10.59 $C_{19}H_{42}Si$. Calculated %: Si 9.42
 $(CH_3)_3Si{-}\underset{CH_3}{CH}{-}CH_2{-}CH_2{-}CH_2{-}CH_3$; B.p. 175-176°; d_4^{20} 0.7517; n_D^{20} 1.4222	
$(n\text{-}C_4H_9)_3Si{-}CH_2{-}CH_2{-}CH_3$; B.p. 267-268°; d_4^{20} 0.7949; n_D^{20} 1.4462	
 $(C_2H_5)_3Si{-}CH_2{-}\underset{CH_3}{CH}{-}\underset{CH_3}{CH}{-}CH_2{-}Si(C_2H_5)_3$; B.p. 314-317°; d_4^{20} 0.8376; n_D^{20} 1.4672	
 $(n\text{-}C_4H_9)_3Si{-}CH_2{-}\underset{CH_3}{CH}{-}CH_2{-}CH_2{-}CH_3$; B.p. 290-290.2°; d_4^{20} 0.8038; n_D^{20} 1.4500	

EXPERIMENTAL

The conditions used in typical alkyl-lithium syntheses are as follows. 51.2 g of β-bromopropyltrimethylsilane was added during 15 min. to 40 g of BuLi, with vigorous stirring; considerable evolution of heat was observed. The mixture was treated with ice and 10% HCl, the ether layer was separated and dried. Distillation gave 9.8 g of β-butylpropyltrimethylsilane (yield 21.8%) and 2 g of 1,4-di-(trimethylsilyl)-2,3-dimethylbutane (yield 5%). Under similar conditions 42.75 g of β-bromopropyltributylsilane and 30 g of BuLi gave 8 g of $Bu_3{-}Si{-}CH_2{-}\underset{CH_3}{CH}{-}CH_2{-}CH_2{-}CH_2{-}CH_3$ (yield 20%) and 2 g of $Bu_3{-}Si{-}CH_2{-}CH_2{-}CH_3$. In addition, a small amount of high b.p. products was obtained, but no individual silanes were isolated. The properties of the asymmetrical monosilanes of the $C_{12}{-}C_{19}$ series obtained are given in Table 2, as well as those of one of the disilanes.

We also attempted the condensation of β-bromopropyltriethylsilane with EtLi, and in this case too the yield of condensation products was about the same as with higher molecular weight radicals, viz., 23.4%, and reduction and condensation products were also found among the by-products.

D. I. Mendeleev Institute of Chemical Technology Received July 31, 1952

LITERATURE CITED

[1] A. D. Petrov and V. F. Mironov, Proc. Acad, Sci. USSR, 75, 707 (1950); 80, 761 (1951); Bull Acad. Sci. USSR, Div., Chem, Sci., No. 4, 635 (1952)*.

[2] K. A. Kocheshkov and V. A. Zasosov, J. Gen. Chem., 16, 777 (1946); H. Gilman and C. Brannen, J. Am. Chem. Soc., 72, 4280 (1950); A. D. Petrov and V. S. Chugunov, Proc. Acad, Sci. USSR 77, 815 (1951) and others.

---

* See Consultants Bureau English Translation, p. 591.

BLANK
PAGE

SYNTHESIS AND PROPERTIES OF UNSATURATED SILICOHYDROCARBONS: DIMETHYLDI-(METHYLALLYL)SILANE, METHYLDI-(METHYLALLYL)SILANE, METHYLTRI-(METHYLALLYL)SILANE, TETRA-(METHYLALLYL)-SILANE, TRIMETHYLCYCLOPENTADIENYLSILANE, AND TRIMETHYLBUT-3-ENYLSILANE

A. D. Petrov and G. I. Nikishin

Whereas there are numerous references in the literature to the synthesis and properties of mono-, di-, tri-, and tetra-allylsilanes [1], it is only recently that Petrov and Mironov [2] reported the synthesis of the first representative of the homologous methylallyl series —triethylmethylallylsilane. Continuing these studies, we prepared silicohydrocarbons with two, three, and four methylallyl radicals. The yields of these silicohydrocarbons, prepared by Grignard synthesis from the appropriate silyl halides and isobutenyl halide by the Yavorsky procedure, ranged from 35 to 45%, and were thus somewhat lower than those of allylsilanes. It was also noticed that these yields were, in the cases of tri- and tetra-methylallylsilanes, obtained only by vacuum fractionation of the reaction products; the yields obtained from distillation at atmospheric pressure were much lower, because of partial thermopolymerization of the methylallylsilanes, giving high b.p. products. It might be concluded that methylallylsilanes enter into polymerization and copolymerization reactions more readily than do allylsilanes.

Trimethylcyclopentadienylsilane and trimethylbut-3-enylsilane were synthesized, for the purpose of making a comparative study of the ease of polymerization of different silicohydrocarbons. The second of these silicohydrocarbons is of additional interest in that it is the first known compound of this class with a double bond in the γ-position. As is known from the literature [3] vinylsilanes are difficultly polymerizable, owing to the effect exerted by the silicon atom, whereas polymerization of allylsilanes proceeds very readily.

Trimethylcyclopentadienylsilane was prepared as follows. Butyl-lithium and cyclopentadiene gave cyclopentadienyl-lithium:

$$LiC_4H_9 + C_5H_6 \longrightarrow C_4H_{10} + C_5H_5Li.$$

This, with trimethylchlorosilane, gave what appeared to be a mixture of 1- and 2-trimethylcyclopentadienylsilane, as appears from the change in its properties when it is redistilled:

$$C_5H_5Li + (CH_3)_3SiCl \longrightarrow (CH_3)_3SiC_5H_5 + LiCl.$$

Trimethylcyclopentadienylsilane (or 1-trimethylsilylcyclopentadiene) was condensed by a Diels-Alder reaction with maleic anhydride, giving an adduct of m.p. 102°. Trimethylbut-3-enylsilane was obtained by the following reactions:

$$(CH_3)_3SiCl + SO_2Cl_2 \longrightarrow (CH_3)_2ClSiCH_2Cl; \quad (1)$$

$$(CH_3)_2ClSiCH_2Cl + CH_3MgI \longrightarrow (CH_3)_3SiCH_2Cl; \quad (2)$$

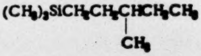
$$(CH_3)_3SiCH_2Cl + Mg \longrightarrow (CH_3)_3SiCH_2MgCl; \quad (3)$$

$$(CH_3)_3SiCH_2MgCl + BrCH_2 \cdot CH = CH_2 \longrightarrow (CH_3)_3SiCH_2CH_2CH = CH_2 \quad (4)$$

Chlorination of trimethylchlorosilane with sulfuryl chloride [4] gave dimethylchloromethylchlorosilane (35% yield), which with CH_3MgI afforded trimethylchloromethylsilane (60% yield), and this gave a Grignard reagent [5], which with allyl bromide yielded $(CH_3)_3SiCH_2CH{=}CH_2$ (65% yield). Since we possessed this product, with the double bond in the γ-position, we thought it would be of interest to ascertain how hydrogen bromide adds on to the double bond.

There are numerous indications in the literature of the nonequivalence of carbon atoms at different distances from the silicon atom, and of alternation of charges along the chain: $\overset{+}{Si}-\overset{-}{C}-\overset{+}{C}-\overset{-}{C}-\overset{+}{C}$. The physicist Fajans [6] considered that such an alternation was indicated by his refractometric studies. Accepting, however, alternation of charges along the chain, we still know nothing of how the magnitude and the distribution of these charges change under the influence of the reacting substances. We know that HBr adds on to trialkylvinylsilane in the opposite way to the Markovnikov rule [2,7], but to trialkylallylsilane according to this rule [8]. HBr also adds on to the double bond in the δ-position according to Markovnikov's rule, as was shown recently [9] for $(CH_3)_3SiCH_2CH(CH_3)CH_2CH{=}CH_2$.

As a result of addition of HBr to the double bond in the γ-position, and of condensation of the bromide with $MgBrC_2H_5$ the silicohydrocarbon (I) was obtained:



$$(CH_3)_3SiCH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{C}H}CH_2CH_3$$

This was shown by the synthesis of the isomeric hydrocarbon (II):

$$(CH_3)_3SiCH_2CH_2CH_2CH_2CH_2CH_3$$

and by the establishment of their different physical properties and Raman spectra. This result shows that alternation of charges causing reversal of the order of addition of HBr to the double bond ceases at the β-position.

EXPERIMENTAL

Synthesis of methylallylsilanes. Isobutenyl chloride was prepared by the method of Kazansky and Lukina [10], about a kg. being obtained.

TABLE

Properties of methylallylsilanes

		Yield in %
$(CH_3)_2Si(CH_2-\overset{CH_3}{C}=CH_2)_2$; b.p. 178-178.5°; n_D^{20} 1.4515; d_4^{20} 0.8012	Found %: C 70.01; 70.26; H 11.71; 11.81; Si 16.06; 16.23; $C_{10}H_{20}Si$. Calculated %: C 71.35; H 11.91; Si 16.67	46
$(CH_3)HSi(CH_2-\overset{CH_3}{C}=CH_2)_2$ b.p. 61-63° at 17 mm; n_D^{20} 1.4550; d_4^{20} 0.7885	Found %: C 68.98; 69.02; H 11.82; 11.67; Si 17.71; 17.94 $C_9H_{18}Si$. Calculated %: C 70.05; H 11.75; Si 18.18	21.3
$(CH_3)Si(CH_2-\underset{CH_3}{C}=CH_2)_3$ b.p. 231.9-232.1° n_D^{20} 1.4772; d_4^{20} 0.8338	Found %: C 75.24; 75.00; H 11.78; 11.67; Si 12.43; 12.40 $C_{13}H_{24}Si$. Calculated %: C 75.00; H 11.54; Si 13.46	35
$Si(CH_2-\underset{CH_3}{C}=CH_2)_4$; b.p. 269.5-270.5° (130-133 at 11 mm); n_D^{20} 1.4950; d_4^{20} 0.8609	Found %: C 76.22; 76.55; H 11.05; 11.20; Si 11.68; 10.95 $C_{16}H_{28}Si$. Calculated %: C 77.4; H 11.3; Si 11.3	40

The synthesis of dimethyldi-(methylallyl)silane and methyldi-(methylallyl)-silane was effected by boiling the substrates in ethereal solution for 20 hrs. Higher temperatures were required for the syntheses of methyltri-(methylallyl)silane and tetra-(methylallyl)silane. After boiling the ethereal solution for 2 hrs the ether was distilled off, xylene was added, and the solutions were boiled on an oil-bath for 12 hrs. The synthesis of the corresponding allylsilanes did not require such drastic conditions (distilling off the ether, and raising the temperature to 130°) [1,2]. The properties of the methylallylsilanes, and the yields obtained are given in the Table.

Synthesis of trimethylcyclopentadienylsilane. Butyl-lithium was prepared from 7.9 g of lithium and 82.2 g of butyl bromide, and 34 g of freshly distilled cyclopentadiene is added dropwise during 40 min. to the ethereal solution, cooling the flask with ice-water, and passing a stream of nitrogen to exclude air. 65 g of trimethylchlorosilane was then added, and the mixture was left overnight, and boiled the next day for 12 hr under reflux. The solution was then filtered off from the white precipitate which forms, and water was added to the filtrate. The product was fractionated, giving 9 g of product, b.p. 138-140°, n_D^{20} 1.4622, d_4^{20} 0.8308. 2.1 g of maleic anhydride was added to a solution of 3 g of this product in 10 ml of ether; the reaction proceeded vigorously, all of the maleic anhydride going into solution within 5 min. After an hour a voluminous precipitate of transparent colorless crystals had formed; the product melted at 102-102.5° after two recrystallizations from ether.

Synthesis of trimethylbut-3-enylsilane. We shall here describe only the final stages of the reaction, which have not previously been reported in the literature. The Grignard reagent prepared from 8.2 g of magnesium and 41 g of trimethylchloromethylsilane was added to a solution of 50 g of allyl bromide in 50 ml of ether. Heat was evolved, and the solution boiled for a short time. The solution was left overnight, and then boiled under reflux for 12 hrs, after which the ether was distilled off, and the residue was heated on a water-bath at 70-80° for 8 hrs.

Fractional distillation gave 27.4 g of trimethylbut-3-enylsilane, b.p. 111.5-112.5°, n_D^{20} 1.4148, d_4^{20} 0.7358, MR_D found 43.66, calculated 43.70. The Raman spectrum was*: 148(2), 207 (5), 247 (2), 271 (1), 324 (3), 521 (3), 577 (3), 588 (9), 616 (4), 637 (3), 692 (6), 899 (1), 940 (3), 1014 (2), 1103 (3), 1173 (3), 1280 (7), 1298 (6), 1415 (8), 1639 (10), 2845 (5), 2897 (20), 2959 (8), 3002 (6), 3080 (5).

The characteristic frequency of the double bond in the γ-position, 1639 cm^{-1}, fits satisfactorily into the series:

1) $\equiv SiCH=CH_2$–1591 cm^{-1}; 2) $\equiv SiCH_2 \cdot CH=CH_2$ 1630 cm^{-1}; 3) $\equiv Si-CH_2-CH_2-CH_2CH=CH_2$ –1642 cm^{-1}.

Saturation of the silicohydrocarbon with HBr gave a bromide, b.p. 64° at 15 mm; n_D^{20} 1.4542; d_4^{20} 1.0894: found MR_D 52.02; calculated MR_D 51.85.

This bromide was added to magnesium ethyl bromide in ether. There was no visible evidence of any reaction, but after distilling off the ether a precipitate formed, with evolution of heat. The product was heated at 100° for 10 hrs, and water was then added. The product was distilled, giving a 22% yield of a product which we identified as trimethyl-3-methylpentylsilane (silicohydrocarbon I), b.p. 154-154.3°, n_D^{20} 1.4170; d_4^{22} 0.7450; found MR_D 53.44; calculated MR_D 53.43. The physical constants of this silicohydrocarbon and its Raman spectrum differ markedly from those of trimethyl-n-hexylsilane (silicohydrocarbon II b.p. 160-162°, n_D^{20} 1.4153, d_4^{20} 0.7422).

Received July 26, 1952

D. I. Mendeleev Institute of Chemical Technology

LITERATURE CITED

[1] L. Sommer, L. Tyler, F. Whitmore, J. Am. Chem. Soc., 70, 2872 (1948); A.D.Petrov and V.F.Mironov, Proc. Acad. Sci. USSR, 75, No. 5, 707 (1950); Amer. Cyanamide Co. U. S. Pat. 2381793 (1945); H. Post, Silicones and Other Organic Silicon Compounds, N. Y. 1949, p. 186; A. D. Petrov and L. L. Shchukovskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 3, 564 (1952).**

[2] A. D. Petrov and V. F. Mironov, Proc. Acad., Sci. USSR, 80, No. 5, 761 (1951).

[3] S. N. Ushakov and A. M. Itenberg, J. Gen. Chem., 7, 2495 (1937); B. N. Yakovlev, J. Gen. Chem., 19, 1969 (1949).***

[4] L. I. Mc Bride, H. C. Beachell, J. Am. Chem. Soc., 70, 2532 (1948).

[5] F. C. Whitmore, L. H. Sommer, J. Am. Chem. Soc., 68, 481 (1946).

[6] H. Fajans, Chem. and Eng. News 27, 900 (1949).

[7] F. C. Whitmore, Chem. and Eng. News, 26, N 10, 668 (1948).

[8] L. H. Sommer, L. L. Tyler, F. C. Whitmore, J. Am. Chem. Soc., 70, 2872 (1948).

[9] A. D. Petrov and V. F. Mironov, Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 4, 635 (1952).****

[10] B. A. Kazansky and M. Yu. Lukina, Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 1, 47 (1951).

---

* I am indebted to Yu. P. Egorov for the Raman spectra.

** See Consultants Bureau English Translation, p. 537.

*** Evidently a typographical Error remains uncorrected in this reference. No report by Yakovlev appears in the Journal of General Chemistry USSR, Vol. XIX, 1949. Publisher.

**** See Consultants Bureau English Translation, p. 591.

BLANK
PAGE

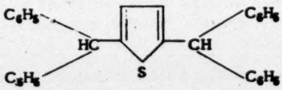
STRUCTURE AND CERTAIN PROPERTIES OF DIBENZHYDRYLTHIOPHEN

Ya. L. Goldfarb and M. S. Kondakova

We know that the reason for the common properties of systems of the type benzene, thiophen, furan, pyrrole, and others has been considered [1] to be their possession of an electron sextet, the so-called aromatic sextet. This schematic representation, which is essentially an electronic interpretation of Bamberger's early views [2], does not take into account a whole series of features of heterocyclic compounds, such as the retention by the salts of some alkylpyrroles of aromatic properties [3], or furan reacting as a diene. It is nevertheless of interest to obtain new experimental data relating to the role of the electron sextet as a carrier of aromatic properties. In this connection a comparison of the properties of thiophen, as an aromatic system, with those of its corresponding sulfone would be instructive; in the latter compound one should expect, on purely formal grounds, that parallel with the loss of aromatic properties the appearance of diene properties would be observed.

Thiophen itself does not form a sulfone; di- and tetra-oxythiophen, described by Lanfry [4], are not sulfones, according to Hinsberg [5] (see also [6] and [7]). To the best of our knowledge there have been no papers published describing the sulfones of alkyl and aralkyl thiophens. This type of sulfone should, however, represent the most suitable material for the present research.

With this object we undertook the synthesis of the sulfone of dibenzhydrylthiophen. Dibenzhydrylthiophen is readily prepared from a mixture of thiophen and benzhydrol or benzhydryl ethyl ether by the action of stannous chloride [8]. From the nature of its formation it follows that substitution must have taken place in positions 2 and 5. This is confirmed by the results of hydrogenolysis, using a Raney nickel catalyst (see experimental section). The hydrocarbon so obtained has the composition and m.p. (122-123°) of 1,1,6,6-tetraphenylhexane $(C_6H_5)_2CH(CH_2)_4CH(C_6H_5)_2$, described by Vorlander et al. [9]; its solubility in ethanol differs from that given by these authors. For this reason we repeated Vorlander's synthesis, using N. M. Kizhner's instead of Klemmensen's method in the reduction of 1,1,6,6-tetraphenylhexa-3,4-dione. Contrary to Vorlander's observation, the hydrocarbon so obtained is relatively sparingly soluble in hot ethanol; its mixed m.p. with the hydrocarbon obtained from dibenzhydrylthiophen shows no depression. The structure of this product may therefore be taken as corresponding with that of 1,1,6,6-tetraphenylhexane, and our dibenzhydrylthiophen must be substituted in the 2,5-position:



(I)

Compound (I) gave the corresponding sulfone when treated with perhydrol, under the conditions described below. This product, like the great majority of sulfones, is not reduced by zinc in hydrochloric and acetic acid, but it is partly converted into 1,1,6,6-tetraphenylhexane by the action of spongy nickel catalyst. It does not give an addition product with excess of maleic anhydride at 200-220° or in boiling nitrobenzene, and it is not acetylated under the conditions for formation of the corresponding ketone from dibenzhydrylthiophen [8]. It reacts very slowly at room temperature with bromine in chloroform solution, without any perceptible evolution of hydrogen bromide; the product contains two atoms of bromine, apparently in the 1,4-positions. Under similar conditions dibenzhydrylthiophen gives a mono-bromo-derivative; since its oxidation products include benzophenone it follows that the bromine atom must be in the thiophen ring.

Thus the addition of two atoms of oxygen to the sulfur atom of dibenzhydrylthiophen involves loss of the tendency of atoms 3 and 4 of the thiophen ring to be substituted by halogen or acetyl, i.e., loss of aromatic properties. At the same time the sulfone does not react as a diene with maleic anhydride.

We do not yet know, however, whether this lack of reactivity with maleic anhydride is a feature of all sulfones of alkyl and aralkyl thiophens, or whether it is due to steric hindrance in the given case only.

EXPERIMENTAL*

1. Hydrogenolysis of dibenzhydrylthiophen. 25 g of spongy nickel catalyst is added to a solution of 5 g of dibenzhydrylthiophen in 100 ml of dry toluene (the catalyst was prepared by Mosingo's method [10]). The mixture was heated to boiling during 4 hrs, and then left overnight. The nickel was then filtered off and washed with several portions of toluene. The toluene was distilled off from the filtrate + washings, leaving about 5 g of crystalline product, m.p. 110-116°, recrystallization of which from ethanol gave two lots of crystals: 1.5 g of m.p. 83-107°, and 2.4 g of m.p. 121-123°, rising to 122-123° after a second recrystallization from ethanol, in which it is sparingly soluble in the hot.

Found %: C 92.18; 92.46; H 7.61; 7.76
$C_{30}H_{30}$. Calculated %: C 92.30; H 7.7

The product gave no depression of m.p. when mixed with 1,1,6,6-tetraphenylhexane (see below).

2. Preparation of 1,1,6,6-tetraphenylhexane. A mixture of 0.5 g of 1,1,6,6-tetraphenylhexa-3,4-dione (m.p. 188-189°; prepared by Vorlander's method), 0.2 g of sodium in 7.25 ml of absolute alcohol, and 1.5 g of hydrazine hydrate solution (56%) was heated at 190-200° for 29 hrs in a small autoclave, and the solid product was separated and mixed with a small amount of water. The mixture was repeatedly extracted with ether, the extract was washed with water, and the ether was distilled off, leaving 0.2 g of residue, m.p. 118-120°, sparingly soluble in hot alcohol. Recrystallization from alcohol gave 1,1,6,6-tetraphenylhexane, m.p. 123-124.5°.

3. Action of perhydrol on 2,5-dibenzhydrylthiophen. 8 g of 28% perhydrol was added at room temperature to 4.16 g of dibenzhydrylthiophen in 25 ml of glacial acetic acid. The precipitate which forms gradually redissolves as the mixture is heated. The temperature was maintained at 104-105° for 25 min., and the solution on cooling deposited 4.5 g of crystalline product, m.p. 158-163°, which after recrystallization from alcohol gave 2.2 g of a product of m.p. 171-173°, raised to 172-173° by further recrystallization.

Found %: C 80.65; 80.60; H 5.50; 5.56; S 7.06; 6.92
$C_{30}H_{24}O_2S$. Calculated %: C 80.35; H 5.35; S 7.14

2,5-Dibenzhydrylthiophen-1,1-oxide is insoluble in alkalis. It is readily soluble in chloroform, benzene, and toluene, soluble in hot alcohol and in hot acetic acid, and sparingly soluble in hot heptane. It is not reduced by zinc with a boiling mixture of hydrochloric and acetic acid.

4. Bromination of 2,5-dibenzhydrylthiophen. A solution of 1.1 g of bromine (0.0068 mol) in 20 ml of chloroform was added gradually to 1.5 g (0.0036 mol) of dibenzhydrylthiophen in 15 ml of chloroform, and the mixture was left at room temperature for 4 hrs, after which the chloroform was distilled off, leaving a resinous residue, part of which was soluble in hot alcohol. A yellow precipitate separated from the alcoholic solution on cooling. This was collected, giving 0.4 g of product, m.p. 125-126°, raised to 127-129° by further recrystallization from alcohol; pale yellow needles.

Found %: C 72.51; 72.25; H 4.79; 4.55; S 6.07; 6.16; Br 16.52; 16.38
$C_{30}H_{23}BrS$. Calculated %: C 72.72; H 4.64; S 6.46; Br 16.16

5. Oxidation of the bromo-derivative of dibenzhydrylthiophen. A mixture of 1.3 g of bromodibenzhydrylthiophen, 3 g of CrO_3, and 65 ml of acetic acid was heated on a water-bath for 4 hrs, the mixture was poured into water, and extracted with ether. The extract was washed successively with 5% aqueous sodium carbonate, 5% aqueous KOH, and water, and dried with $MgSO_4$. The ether was distilled off, leaving 0.75 g of an oil, which crystallized when seeded with a crystal of benzophenone. The redistilled product melted at 42-44°, mixed m.p. with benzophenone 44-46°.

6. Reduction of 2,5-dibenzhydrylthiophen-1,1-dioxide. A solution of 1.2 g of the dioxide in 10 ml of toluene was added to a flask containing 40 ml of dry toluene and nickel catalyst prepared by Mosingo's method [10], and the mixture was boiled, with stirring, for 7 hrs., after which it was filtered, and toluene was distilled off from the filtrate. The residue crystallized after addition of a small amount of heptane. The product was extracted with hot benzene-heptane mixture, and the solution was filtered off from insoluble residue. After standing, the filtrate deposits three crops of crystals, The first consisted of unchanged dioxide, and the other two (0.25 g), m.p. 117-125°, of a hydrocarbon, which after recrystallization from alcohol, melted at 122-123°, not depressing the m.p. of 1,1,6,6-tetraphenylhexane.

---

* With Z. V. Volodina.

7. Bromination of 2,5-dibenzhydrylthiophen-1,1-dioxide. A solution of 0.5 g of bromine in 3 ml of chloroform was added to a solution of 0.6 g of 2,5-dibenzhydrylthiophen-1,1-dioxide in 6 ml of chloroform. The mixture was kept at room temperature for 6 days, during which time evolution of hydrogen bromide was not observed. The chloroform was then distilled off in vacuum, leaving a pasty brown mass, which was heated with heptane. The powdery substance so obtained was recrystallized from benzene-heptane mixture, giving a product melting at 191-191.5°, sparingly soluble in alcohol and heptane, readily soluble in benzene and toluene. Boiling the bromo-derivative with zinc in hydrochloric acid-acetic acid mixture gives a bromine-free product, m.p. 172-173°, not depressing the m.p. of 2,5-dibenzhydrylthiophen-1,1-dioxide.

Found %: C 59.08; 59.18; H 4 33; 4.12

$C_{30}H_{24}Br_2O_2S$. Calculated %: C 59.21; H 3.94

Received July 12, 1952

Institute of Organic Chemistry
Academy of Sciences USSR

LITERATURE CITED

[1] J. W. Armit and R. Robinson, J. Chem. Soc., 127, 1604 (1925).

[2] E. Bamberger, Ber., 24, 1758 (1891).

[3] H. Gilman, Organic chemistry, 2nd ed., No. 1, p. 127.

[4] M. Lanfry, Comptes. rend. 156, 73 (1911); 154, 1090 (1912).

[5] O. Hinsberg, Ber., 48, 1611 (1915).

[6] W. Steinkopf, Ann., 430, 96 (1923).

[7] H. J. Backer, J. L. Melles, Proc. Roy. Acad. Sci., Amsterdam, B. 54, 340 (1951).

[8] Ya. L. Goldfarb, J. Russ. Phys. Chem. Soc., 12, 1073 (1930).

[9] D. Vorlander, E. Rack, W. Leister, Ber., 56, 1135 (1923).

[10] R. Mosingo, Org. Synth., 21, 15.

BLANK
PAGE

CONFERENCE ON THE CHEMISTRY AND PHYSICAL CHEMISTRY OF HIGH-MOLECULAR COMPOUNDS

The VII Conference on the Chemistry and Physical Chemistry of High Molecular Compounds, held in Moscow on the 9-12 July 1952, was one of the most characteristic features of the successful development in the USSR of the still relatively young science of the synthesis and properties of organic compounds of high molecular weight. Nine years have passed since the first Conference was held, and during this relatively short period the Academy of Sciences USSR has held seven conferences, each of which was characterized not only by its thematic program but also by being a milestone on the path of our advancing knowledge of high molecular compounds. In contrast to the VI Conference held on the 21st of June, 1949 in Leningrad, the VII Conference included extensive scientific discussion and criticism relating to all the basic problems of structure and properties of high molecular compounds, in which not only well known specialists in this field participated, but also numerous young scientists from industrial institutes and establishments, belonging to the chemical, light, paper and timber, agricultural machinery, aviation, and other industries.

The VII Conference was devoted to the general problems of the chemistry and physical chemistry of natural and synthetic high molecular compounds, of which synthetic rubber and cellulose were the most important. This was the first conference at which researches on plastics were comparatively well represented, their absence from earlier conferences being ascribable to the inadequate scale of scientific work in the field. Another novel feature of the proceedings was a small number of papers on artificial fibers and materials for their manufacture, consisting of carbo- and hetero-chain high molecular compounds. The rapid growth in the number of new high molecular compounds and in their applications, during the past few years, and the intensification of scientific research on earlier known compounds of this group have led to the broadening of the range and dimensions of the work of these conferences.

The VII Conference may be considered to have been the one with the biggest program and the largest number of members. The new stage in development of knowledge relating to high molecular compounds in the USSR, and the close connection between the purely scientific aspects of this field and its practical aspects and the needs of industry, are illustrated by the following statistics. 46 papers were read at the Conference (and many more were submitted), from 27 scientific research institutes, both of the Academy of Sciences and of industrial ministries. Over 500 persons attended the Conference, from 42 scientific research institutes, 28 educational establishments, 32 enterprises, and 4 Republican Academies of Science.

The successful management of a conference with so broad a program and so numerous a membership was due firstly to the new method (introduced at the VI Conference) of organization, involving the prior publication* of the full text of the papers to be read, and their dispatch in good time to Conference members; this method was initiated by the Division of Chemical Sciences of the Academy of Sciences USSR. In this way there was no real need for the authors to read the papers, and nine tenths of the time could be devoted to discussion of the papers; the points made by those taking part in the discussions were in most cases also prepared well in advance, and were for this reason the more effective. In this way over 150 persons were able to engage in the discussions during the four days of the Conference, in addition to the authors themselves, who were allowed five minutes to introduce their papers, as well as to take part in the discussions.

The papers read at the Conference were devoted to the following basic problems of present day high polymer science:

1. Mechanism of synthesis and reaction of formation kinetics.

2. Chemical structure and its relation to properties of high polymers.

3. Physical structure and its connection with the physico-chemical properties of natural and synthetic high molecular compounds.

The most characteristic feature of the Conference was that the discussions were devoted less to a considerat of the actual experimental material presented in the papers than to general problems of the chemistry and physical chemistry of the processes leading to the formation of the high molecular compounds, and to their properties, as elucidated by the experiments. The discussions centered largely around the mechanism of reactions of formation of high polymers, in particular relation to the role of the action of various substances in initiating reactions of polymerization and polycondensation. Other topics debated were the connection between the chemical and physical strucutres of high molecular substances and their properties, in particular the specific features of the phase state of crystalline and amorphous substances, and the nature of their highly elastic deformations in the vitreous and crystalline state.

---

* Chemistry and physical chemistry of high molecular compounds (Collected papers of the VII Conference). Published by the Acad. Sci. USSR, 1952.

In the discussions the greatest interest attached to the problem of the significance of chemical and physical structural factors for the evaluation of the useful properties of actual plastics made from natural and synthetic high molecular compounds. The importance of this problem is particularly great when it is approached in the light of A.M. Butlerov's teachings on the interconnection between the structure of a substance and its properties, and also in view of the important role played by intermolecular action, and by the forces determining this action, in determining the properties of substances of high molecular weight. A large group of papers, and much lively discussion, were devoted to the chemical researches presented by V V. Korshak, S.N. Ushakov, M.F. Shostakovsky, T I. Yurzhenko, G.S. Petrov, V.I. Sharkov, Z.A. Rogovin, and other known workers in this field.

The discussion of these papers, most of which were new and original, gave rise to a number of quite interesting generalizationsand conclusions, which opened up broad perspectives of further researches, not only in the field of the synthesis of new commercially important high molecular compounds, but also in that of the more effective study of the processes of their formation and of the properties, based on a study of their constituent chemical units.

The physico-chemical group of papers was much more broadly represented at the Conference, and they gave rise to particularly animated and fruitful discussion. To this group belonged, in the first place, the papers submitted by the following, together with their collaborators: P.A. Rebinder, A.P. Pisarenko, B.A. Dogadkin, K.T. Poroshin, A.S. Kuzminsky, V.I. Kasatochkin, and others. There emerged from these papers and from their discussion new and original approaches to the study of the complex physico-chemical phenomena of the building up and degradation of high molecular compounds, of practical importance in the processing of rubbers, plastics, and other industrially important materials. The phenomena of vulcanization of rubber, and of other of its transformations were taken as the basis for the drawing of further theoretical conclusions as to the significance of chemical and physical factors for the formation and the stability of actual structures of high molecular straight chain compounds.

An equally important place was occupied in the proceedings of the Conference by a numerous group of papers relating to the structure and the physico-mechanical properties of crystalline and amorphous high molecular compounds. Papers were presented, among others, by the following well-known scientists and their collaborators in this field: V.A. Kargin, V.N. Tsvetkov, S.N. Zhurkov, S.N. Sokolov, B.A. Dogadkin, Yu.S. Lazurkin, G.M. Bartenev, and others. Three basic problems of the structure and mechanical properties of high molecular compounds emerged from these papers and from their discussion from different points of view, based on different methodic approaches:

1. The nature of extreme deformations, and of the resulting mechanical properties, of amorphous high molecular compounds in the vitreous state.

2. The nature of the crystalline structure of high molecular compounds and the reasons for the manifestation of relaxational properties when these substances are deformed.

3. The thermodynamics of the highly elastic deformation of high molecular compounds, and, in particular, the role of the entropic and energetic terms of the equation of state of these compounds.

It will readily be seen that these questions can be reduced to one common property of all high molecular compounds, whether crystalline or amorphous, which differentiates them from low molecular substances in analogous states; this is the presence of two structural elements, and hence of two derivatives in the structure-forming and mechanical behavior of these compounds — the molecules as a whole, and their constituent units.

This feature of high molecular compounds is the basic factor determining their very valuable property, of great theoretical and practical interest, of combining high mechanical strength with high tensile deformability, which is not encountered in the physics of low molecular bodies. The specific nature of their physico-mechanical properties is revealed clearly not only in amorphous high molecular glasses, but also in crystalline high molecular compounds, which, as we know, differentiates them sharply from low molecular glasses and crystals.

During the discussions the essential task of scientific workers in this field was clearly formulated. This is to concentrate their attention not on the study of extreme structural modifications of crystalline or amorphous high molecular compounds, but rather on the study of the actual structures of these bodies, and on the nature of their deviations from the limiting states, known as "structural defectiveness", which is responsible for differences in their physico-mechanical properties, and for their behavior under working conditions. With this are also apparently bound up the causes for the low value of the energetic term of their equation of state in the deformation of high molecular bodies, illustrated by the example of unstressed rubbers.

Finally, the VII Conference, in fulfilment of the resolutions of the preceding Conference, debated, and in general approved of, the project of the systematics and nomenclature of the chemical structure of high molecular compounds drafted by a Commission presided over by Professor V.V. Korshak. This rational nomenclature is based on the structure of the principal chain of the macromolecule. The prefix "poly" indicates the high molecular nature of a compound. After this prefix is placed a square bracket, within which are placed the number and positions of the substituents with the corresponding designation of the molar proportion of each of them, and in parentheses is given the name of the basic recurrent unit of the chain. Examples of the application of this rational nomenclature to generally known high molecular compounds are:

1. Polystyrene — poly[phenyl(ethylene)].
2. Polyvinyl chloride — poly[chloro(ethylene)].
3. Polyvinylidene — poly[1,1-dichloro(ethylene)].
4. Rubber — poly[2-methyl(butenylene)].
5. Vinyon — (copolymer of vinyl chloride and vinyl acetate) — poly(75 chloro(ethylene) 25 acetoxy(ethylene))].
6. Polycaprolactam (caprone) — poly[aminocaprolein].
7. Polythene — poly(methylene).

This great and fruitful work of Soviet scientists can, of course, be considered to be only the initial stage of the elaboration of a new and rational nomenclature and systematics of the chemical structure of high molecular compounds, but it already allows one to visualize the diversity of this new class of organic compounds, the possibility of the existence of which emerges from A.M Buterlov's teaching of the structure of chemical molecules. A simple comparison of the infinite number of possible compounds with the small number of them known to us today shows how illimitable a field of activity lies in the study of the chemistry of high molecular compounds.

The Conference recorded the priority of the Soviet Union in attacking this problem, which was first considered at the VI Conference in 1949.

At the closing session the Conference enthusiastically endorsed a message of greeting to the great leader and teacher, the friend of Soviet science, Comrade I.V. Stalin.

The resolutions of the VII Conference, summarizing its work, are given below.

RESOLUTION

of the VII Conference on high molecular compounds, held in Moscow on the 9-12 June 1952, on the proceedings of the Conference.

1. The VII Conference on the chemistry and physical chemistry of high molecular compounds considered 46 papers, devoted to general questions of the theory of the structure and properties of the more important polymers — rubbers, plastics, natural and synthetic fibers. A broadly based survey of the basic chemical and physico-chemical rules determining the mechanism of polymerizational and polycondensational processes, the vulcanization of rubbers, and the mechanical qualities of actual high molecular compounds, demonstrated the considerable extension of the scale of scientific research work on polymers in progress in the Soviet Union.

2. In view of the fruitfulness of the discussions on the previously published papers, this procedure having first been adopted at the previous, VI Conference on high molecular compounds, the VII Conference took note of the usefulness of this arrangement, and recommended its continued application.

3. The VII Conference places on record the following resolutions, which emerged from the discussions of the papers.

(1) In view of the importance for their practical application of the mechanical properties and of the nature of structural transformations of polymers, and also in view of the existence of different points of view as to the nature and interconnections of these phenomena, bearing also in mind the need for the further development of the theory relating structure and properties of polymers, the Conference recommends the holding within the nearest future of a symposium devoted to the discussion of the nature of the elasticity and thermodynamics of rubberlike polymers.

(2) The Conference admits the urgent need for broadening the methodic approach to the study of hydrolytic and other chemical transformations of cellulose, taking into account the correlation between chemical and physical factors.

(3) In view of the discussion of M.F. Shostakovsky's paper on the mechanism of decomposition of benzoyl peroxide in the polymerization process, the Conference recommends that the experiments be repeated by the joint efforts of the laboratories concerned, in the Institute of Organic Chemistry, Academy of Sciences U.S.S.R., and the Karpov Institute of Physical Chemistry.

(4) In connection with the large amount of important experimental material dealing with chemical and physico-chemical transformations of cellulose which has accumulated, and also in view of the tasks imposed by the Party, and the Government on the cotton industry, the Conference considers it desirable to hold a symposium in 1953, on the chemistry of cellulose and cotton.

4. The Conference considers that the experiment of conducting extensive open discussion at periodic conferences on high molecular compounds should be continued, with the difference that the next conference should include a limited number of program papers to be read by leading specialists in this field.

5. Succeeding periodic conferences on the general problems of the physics and chemistry of polymers are to be held biennially.

The VIII Conference is to be called before the end of 1953. As before, the papers are to be published before the Conference assembles in a special issue of one of the chemical journals of the Academy of Sciences.

6. The Conference approves the holding of symposia on particular themes, in order to achieve a more concrete discussion of basic scientific and technical trends.

7. The VII Conference, having heard and considered Professor V.V Korshak's paper on the systematics and nomenclature of the chemical structure of high molecular compounds, presented by him on behalf of the Commission on High Molecular Compounds, approves in principle of their project.

The Conference considers it necessary to put on record that the priority for launching this project belongs to the Soviet Union, having been proposed at the VI Conference in 1949, and it underlines the originality of a number of basic principles included in the project.

8. The VII Conference invites the Commission appointed for the consideration of this project, consisting of Prof. V V. Korshak, Chairman, and Prof. B.A. Dogadkin, Prof. B.A. Dolgoploska, Associate Member Academy of Sciences, S N. Danilov, Prof. B.N Rutovsky, Cand. Chem. Sci. G.S. Kolesnikov (members) to take into consideration all the remarks made at the Conference, and to publish their report in the Bulletin of the Academy of Sciences, U.S.S.R., Division of Chemical Sciences, and in "Advances in Chemistry", in order to permit of the discussion in these journals of the details of the project, and of the more precise formulation of its basic propositions, during a period of six months.

After this time, the Commission of High Molecular Compounds is to finalize the new nomenclature and systematics, and to work out ways for their application.

9. In view of the successful outcome of the work on the systematics and nomenclature of the chemical structure of polymers, and bearing in mind the timeliness of conducting analogous work on the physics and physical chemistry of polymers, the Conference appoints a Commission under the chairmanship of Prof. B.A. Dogadkin, consisting of Associate Member Acad. Sci. U S.S.R. A.P. Aleksandrov, Prof. V.N. Tsvetkov, Dr. Chem. Sci. Kh. S. Bagdasaryan, Dr. Chem Sci. G.L. Slonimsky, Prof. S.S. Voyutsky, Prof. S.I. Sokolov, and Cand. Chem. Sci. Yu. M. Malinsky.

This Commission is to complete its work during the period between the VII and the VIII Conferences and they are to submit the results of their work, in the form of a draft project of the H.M.C. Commission, for the consideration of the VIII Conference on High Molecular Compounds.

10. The Conference underlines the timeliness and the urgent need of establishing an academic journal devoted to the chemistry and physics of high molecular compounds, and it asks the H.M.C. Commission to take the necessary steps with the Division of Chemical Sciences and the Praesidium of the Academy of Sciences, U.S.S.R., with the object of issuing this journal as from January 1, 1953.

11. The H.M.C. Commission is asked to consider the possibility of preparing and publishing papers on the history of the development of the science of high molecular compounds in the Soviet Union.

BLANK
PAGE

GENERAL MEETING OF THE DIVISION OF CHEMICAL SCIENCES
OF THE ACADEMY OF SCIENCES U.S.S.R.
TO CELEBRATE THE 75th BIRTHDAY OF ACADEMICIAN A. E. ARBUZOV

A general meeting of the Academy of Sciences Division of Chemistry was held in Moscow on the 23rd September 1952, to celebrate the 75th birthday of that eminent chemist and social worker Aleksandr Yerminingeldovich Arbuzov.

The meeting was opened by the Academician-Secretary of the Division of Chemical Sciences of the Academy of Sciences U.S.S.R., Academician M.M. Dubinin, who spoke of the importance of the scientific, pedagogic, and social activities of Academician A.E. Arbuzov, making the following remarks: "Being a pupil of the famous Kazan school of chemistry, he has for over 50 years honorably borne the glorious banner of Russian science. He is a worthy continuer and preserver of the traditions of this remarkable school; he has himself created an important school of chemistry, in which organic synthesis occupies a leading place. Physical methods have also found an important place in the work of this school. Arbuzov's work on the history of Russian chemistry is of considerable value. He has done very much for the preparation of younger generations of scientists. The whole of Arbuzov's activities are an example of tireless work, of devotion to science, to the nation, and to the aims of the party of Lenin-Stalin."

Papers were read at the meeting, by Academician A.E. Arbuzov, on "Cyclic esters of phosphorous acid," by Associate Member Acad. Sci. U.S.S.R. B.A. Arbuzov, on "The Work of A.E. Arbuzov and his school on organic phosphorus compounds, during the past five years," and by Prof. A.N. Pudovik, on "A new synthesis of phosphinic and thiophosphinic esters".

It was 50 years ago when A.E. Arbuzov, who was then at the beginning of his scientific career, first began work on the sturctureof phosphorous acid and its organic derivatives. The problem had then barely been touched on, and was in a state of confusion. He decided to make this the subject of his independent research work, and applying A.M. Butlerov's theory of chemical structure to the problem of the structure of phosphorous acid and its derivatives, young Arbuzov was able brilliantly to fulfill his task. The work of A.E. Arbuzov and his collaborators developed into a branch of organic chemistry of great theoretical and practical interest. A particularly detailed study was made of those syntheses and reactions in which tervalent phosphorus derivatives were converted under certain conditions into derivatives of quinquevalent phosphorus, and this reaction is now known as the Arbuzov rearrangement. Thousands of phosphorus-organic compounds have since been synthesized, and over 300 cases of the Arbuzov rearrangement are known.

In his paper A E. Arbuzov reported the results of research in the field of so-called cyclic esters of phosphorous acid, hitherto unknown, of which a large number have now been synthesized, including many which are of practical importance. Some of them have powerful insecticidal properties, and may find application in the struggle against crop pests, and a number of them exert a powerful physiological action on mammals, and may become of value in medical practice.

Numerous cyclic esters of phosphorous acid, as well as the products of their rearrangement, are as yet of theoretical interest only, but there can be no doubt that some of them will find practical applications.

Associate Member of the Academy of Sci. U.S.S.R. B.A. Arbuzov reviewed the more important themes pursued by A.E Arbuzov during the past five years. The basic theme was the study of esters of phosphorous acid, and of their Arbuzov rearrangement, as a result of which numerous new compounds were obtained, including absolutely new types of phosphorus-organic compounds, with phosphorus-tin and phosphorus-silicon bonds. A.E. Arbuzov and his pupils showed the profound similarity that exists between phosphorus-organic compounds and purely organic ones.

A considerable advance in the synthesis of phosphorus-organic compounds was the discovery of new methods for the synthesis of diverse phosphinic acids by addition of dialkylphosphorous acids to unsaturated compounds, aldehydes, and ketones. A. E. Arbuzov was the first to prepare esters of hypophosphoric acid and pyrophosphorous acid, in 1930, and was the first to prepare esters of pyrophosphorous acid in a pure form. The latter possess good insecticidal properties, and are of practical interest.

During the past five years intensive research work has been in progress on phosphorus-organic insecticides, at the Institute of Chemistry of the Kazan Filial of the Academy of Sciences USSR, while at the A. M. Butlerov Institute of Chemistry, Kazan University, extensive research has been done on complex compounds of esters of phosphorous acid, and on the application of physical methods to the study of organic derivatives of phosphorus and of other organic compounds.

The attack on organic derivatives of phosphorus is being conducted by Academician A. E. Arbuzov on a broad front. This subject is still far from being exhausted, and promises to yield much more of interest, both theoretically and practically.

Prof. A. N. Pudovik described a new method for the synthesis of esters of phosphinic and thiophosphinic acid, depending on the addition of dialkylphosphorus, dialkylthiophosphorous, and aryl- and alkyl-phosphinous acids to unsaturated electrophilic compounds in presence of alkaline catalysts. Addition of dialkylphosphorous and dialkylthiophosphorous acids to various $\alpha\beta$-unsaturated ketones gave high yields of esters of ketophosphinic and ketothiophosphinic acids, and to $\alpha\beta$-unsaturated aldehydes gave esters of unsaturated oxyphosphinic and oxythiophosphinic acids. Addition takes place at the double bond in the former case, and at the carbonyl group in the latter. Addition of dialkylthiophosphorous acid to saturated aldehydes and ketones gave various esters of oxythiophosphinic acids. Addition of dialkylphosphorous, dialkylthiophosphorous, and aryl- and alkyl-phosphinous acids to esters of unsaturated carboxylic acids gave good yields of phosphonecarboxylic acid esters, of various structures. Dialkylphosphorous and dialkylthiophosphorous acids readily add on to esters of unsaturated dicarboxylic acids (maleic acid and austylenedicarboxylic acid), giving esters of phosphone- and diphosphone-succinic acid. Dialkylphosphorous and dialkylthiophosphorous acids in presence of alkaline catalysts very readily add on to unsaturated cyanides, to esters of unsaturated alcohols, and to esters of ethylidene- and benzylidene-malonic acid and of acetoacetic acid. A new synthesis of aminophosphinic esters was worked out, depending on addition of dialkylphosphorous acids and other phosphorus acids to imines. It was shown that esters of phosphinic acids of different structures can be obtained by the addition of various nucleophil reagents (ammonia, amines, hydrogen sulfide, mercaptans, dialkylphosphorous acids, malonic, acetoacetic, and cyanoacetic esters and their homologs, etc) to esters of vinylphosphinic acid. Altogether over 150 new compounds have been obtained by the application of the new method for the synthesis of phosphinic and thiophosphinic esters.

All three papers aroused considerable interest, as was evidenced by the large number of questions put to the speakers, and by the animated discussions which followed the papers. The following took part in the discussions: Academicians V. M. Rodionov and M. M. Dubinin, Associate Members of the Academy of Sciences USSR V. I. Spitsyn, I. A. Kazarnovsky, S. Z. Roginsky, B. V. Nekrasov, and others.

Numerous letters and telegrams of congratulation were received by A. E. Arbuzov on his birthday. Greetings arrived from the Praesidium of the Academy of Sciences USSR, the Division of Chemical Sciences of the Academy, the Minister of Higher Education, Moscow State University, Kazan State University, the Council of the Filials and Bases of the Academy of Sciences USSR, the Kazan Filial of the Academy of Sciences USSR, the Kazan Institute of Chemical Technology, the Karpov Institute of Physical Chemistry, the Kurnakov Institute of General and Inorganic Chemistry of the Acad. Sci. USSR, the Institute of Physical Chemistry of the Acad. Sci. USSR, the Institute of Organic Chemistry of the Acad. Sci. USSR, the Institute of Organic Chemistry of the Acad. Sci. USSR, the Institute of the History of the Natural Sciences of the Acad. Sci. USSR, the Institute of the History of Chemistry, the All-Union Society for the Dissemination of Political and Scientific Knowledge, the D. I. Mendeleev All-Union Chemical Society, the Chemical Laboratory Ware Factory, the Lenin Works, the Editorial Board of the journal "Nature", and others.

The D. I. Mendeleev All-Union Chemical Society presented A. E. Arbuzov with the Diploma of Honorary Member of the Society.

MEETING OF THE COMMISSION FOR THE EDITING OF D. I. MENDELEEV'S SCIENTIFIC LEGACY AND THE PUBLICATION OF HIS WORKS

The first plenary meeting of this Commission, which had been created by the Praesidium of the Academy of Sciences, U.S.S.R., was held on the 26 September 1952, under the Chairmanship of Academician A.V. Topchiev, with Academicians M M. Dubinin and A.N. Terenin, Associate Member Acad. Sci. U.S.S.R P. Ya. Kochin, Vice-Minister of Higher Education M A Prokofiev, Associate Member Acad. Pedagogic Sci. B.M Kedrov, Professors S.A. Shchukarev, M.P. Vukalovich, and A.V. Storonkin, Doctors, Chem. Sci. K.T. Poroshin and V.P. Barzakovsky, and Docent Yu. K. Novodranov as members. A number of different specialties were represented on this Commission, corresponding to the diversity of D.I. Mendeleev's scientific interests.

The Praesidium of the Academy of Sciences entrusted the Commission with the task of coordinating and editing Mendeleev's scientific legacy, and of publishing his selected works, as well as of publishing new documentary material. At the same time the scope of the D.I. Mendeleev Historical Museum at the A.A. Zhdanov Leningrad State University, where all the documentary material relating to Mendeleev is to be concentrated (partly in the form of photostat copies), is to be considerably widened.

Previously published collections of Mendeleev's works have not taken into account corrections and important additions made by him to his published papers. Even the scanty documentary material which has been published has suffered from distortion of his text and of his meaning. The investigators of Mendeleev's creativity are confronted with a vast textological study, involving a scrupulous deciphering of his manuscripts.

The Commission discussed the preparations for publication of the volume containing new material relating to the discovery of the periodic law and of its formulation. B.M. Kedrov, who reported on this matter, said that during the past three years Mendeleev's daughter, M.D. Mendeleeva (now deceased), T.S. Kudryavtseva, and B. M. Kedrov had found and processed a large number of documents written by Mendeleev, relating to the period from February 1869 to July 1871; it was at this time that he worked out and completed his work on the periodic table of the chemical elements.

These materials include the following: 37 different variants of the table of chemical elements, expressing the periodic relationship of the properties of elements to their atomic weight, more than 20 as yet unpublished manuscripts, of which particular importance attaches to his hitherto unknown papers: "Towards a system of the elements" (autumn 1870), "On certain so called molecular compounds" (late 1871), and "On polymerization in mineral substances" (autumn 1871), 28 minor notes, rough drafts, and research programs, 7 letters and memoranda relating to work on the periodic law.

Considerable interest attaches to the hectographed scripts of Mendeleev's lectures on inorganic chemistry (40 pages), read by him during the winter of 1870-71, and of particular importance is his scientific diary, the first 65 pages of which are a record of his thoughts on the periodic law, and contain outlines of his public lectures on the philosophic aspects of chemistry and of the natural sciences in general.

The compilers of the collection have divided up this material into 19 thematic publications, which present in chronological order Mendeleev's work on the periodic law during 1869-71.

Throughout these papers can be traced Mendeleev's constant aim towards perfecting his periodic system of the elements, towards bringing his great discovery to its full completion. B.M. Kedrov shows that Mendeleev achieved this end in three closely interconnected ways. The first and most important was the branching of the long periods, so converting the long table into a short, eight group table, in which the odd and even periods fall into a system, which greatly facilitates the detailed explanation of the nature of the periodic dependence of properties of elements on their atomic weight. His second approach consisted in investigating the dependence of various properties on atomic weight. Thus, in February 1869, a year before L. Meyer, Mendeleev described the general form of the atomic volumes curve. Finally, the third way of perfecting the periodic table depended on the inclusion within it of elements not previously included and of changing the places of elements in accordance with their changed atomic weights. At the same time, and in the earliest outlines of the system, Mendeleev describes the properties of as yet unknown elements which should fill vacant places in the system.

The new materials show that at the very inception of his discovery of the periodic law Mendeleev arrived at the supposition that an element must exist between hydrogen and lithium, with an atomic weight of 2, of atomic weight 20-21 between fluorine and sodium, and of atomic weight 36 between chlorine and potassium. It was much later that the inert gases helium, neon, and argon, with atomic weights close to those predicted by him were discovered.

The new manuscripts, which are to comprise the first volume of "D.I. Mendeleev, scientific documents" are evidence that Mendeleev had made a number of profound scientific predictions, the existence of which was not known previously. The material under publication allows the reader to penetrate into Mendeleev's very laboratory, to follow, in some cases in the minutest detail, how his great discovery was prepared, and how it developed. Prof. Kedrov spoke of the great difficulties which the compilers of the collection had to overcome in reading the manuscripts and in fixing their dates.

All those who took part in the preparation for publication of these new materials of Mendeleev emphasized the great value and the timeliness of their publication. Associate Member Acad. Sci. U.S.S.R. A.F. Kapustinsky, in speaking of the gigantic task fulfilled by Mendeleev, as a result of which he discovered a most important law of nature, said that there were no extensive researches being conducted at present in the Institutes of the Academy of Sciences on the development and extension of the periodic law. Our task is now not only to study Mendeleev's creative work but also to continue the more important chemical researches begun by Mendeleev in connection with the working out of the periodic law. This is particularly indicated at the present time, in view of the tendency which can be seen in capitalist countries to minimize the importance of Mendeleev's contribution, and to link the periodic law with the names of other authors. Kapustinsky considers that the publication of Mendeleev's works should comprise a uniform series of volumes all of the same format and appearance.

Academician A.E. Arbuzov considers it necessary to study Mendeleev's views on the structure of chemical compounds. A more detailed study needs to be made of the mutual relations of those two Titans of chemical thought, D.I. Mendeleev and A.M. Butlerov. It is of importance that the commentaries which will be given in the Collection should as far as possible acquaint the reader with the trend of Mendeleev's thought. In addition to the commentaries on the documentary material a general review of the development of the periodic law must be given.

Prof. M.P. Vukalovich remarked that Mendeleev had done much work in the fields of thermodynamics and energetics. He was the first to give a definition of critical temperature, and he conducted numerous researches on the critical state, and devised apparatus for such researches. Mendeleev also did important work on fuels, in particular on the underground gasification of coal. Vukalovich thinks it would be useful to publish a separate volume devoted to Mendeleev's work in the fields of thermodynamics, fuels, thermotechnics, and energetics.

Academician M. M. Dubinin considers that the book on Mendeleev's work on the periodic law should have a title which indicates its contents.

Dr. Chem. Sci. K.T. Poroshin said that many books published in the U.S.S.R. (particular translations) did not sufficiently clearly connect the periodic law with the name of its discoverer, D.I. Mendeleev, and he thinks it necessary to produce several types of publication: (a) selected works of Mendeleev, in 5-6 volumes, (b) a few volumes of the series "Classics of Science", (c) collections of new documentary material, and (d) popular scientific literature, dealing with the separate aspects of Mendeleev's activities.

Contributions to the discussion were also made by Associate Member Acad. Sci. U.S.S.R. N.A. Izgaryshev, Dr. chem. Sci. V.N. Barzakovsky, and T.S. Kudryavtseva.

Academician A.V. Topchiev said in his introductory address that the new material on the periodic law gives us an immeasurably more complete picture of the profundity of the theoretical thinking of our great scientist. A study of Mendeleev's legacy should encourage our Soviet scientists to undertake theoretical research, which could raise our knowledge of natural sciences to a higher level. Groups of theoreticians should be formed in the Institutes for work on the general problems of science. Mendeleev was a great theoretician, whose views and thoughts are to this day a guiding thread in the elucidation of important branches of modern theoretical natural science. A vast amount of experimental material has been accumulated in our numerous laboratories, and it now needs to be generalized and considered from the point of view of theory.

It is essential that Mendeleev should become known to the broad masses. The Commission should, in addition to its editorial activities, organize lectures on the activity of Mendeleev. The Commission proposes to hold its meetings in Moscow and Leningrad. Academician A.V. Topchiev concluded his remarks with the hope that the number of those studying Mendeleev's creative work will now rise considerably, and that we shall be able to reconstitute a full image of this great scientist.

ERRATUM

In the paper by V. N. Sveshnikova in the 1952, No. 1 issue of this journal, there is an error, committed by the author, in crystallo-optical constants: on English page 46, on the 12th line from the bottom, Ng = 1.568 is written; this should read Ng = 1.586.